# APPLICATIONS OF TIME-RESOLVED SPECTROSCOPY TO SPECTROCHEMICAL ANALYSIS

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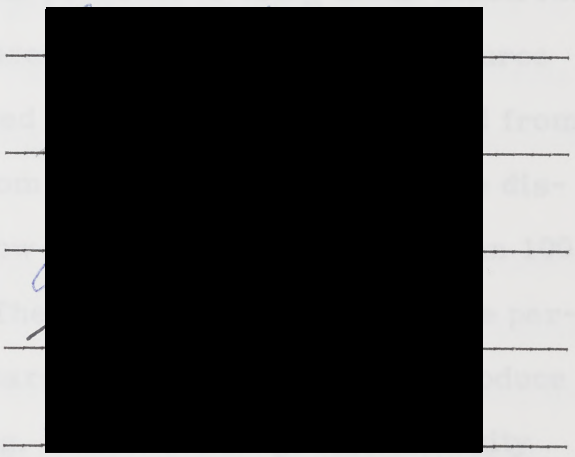

# APPLICATIONS OF TIME-RESOLVED SPECTROSCOPY TO SPECTROCHEMICAL ANALYSIS

A

DISSERTATION

Presented to the Faculty of the Graduate School of

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By

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## PREFACE

A study of several spark techniques of spectrochemical analysis was made using time-resolution as the basis for correlations. Particular emphasis was placed on improving the limits of detection attainable with the graphite spark technique, as well as procedures using metal electrodes. Rotating devices, mirror and disk, were used to trigger a spark source precisely and produce the time-resolved spectra. The light emitted from the sample materials was observed from the time of initiation of the discharge to the diminution of the afterglow light which was greater than 100 microseconds in some applications. The precisely triggered source permitted the superposition of many discharges which singly did not produce enough light for photographic recording. Line-to-background intensity ratios for total light and time-resolved exposures were used to establish the effects of the gaseous atmosphere, electrode sample composition, pressure, and various source parameters. The behavior of the element line intensities, background intensities, and the line-to-background intensity ratios showed the advantages of time-resolution techniques. Excitation of samples was carried out under controlled atmosphere conditions which were generally free of nitrogen to eliminate cyanogen formation. Excitation in binary mixtures containing oxygen showed the effect of oxygen on the sample volatilization behavior and the intensity of background

radiation. Absolute sensitivities from $10^{-8}$ to $10^{-10}$ grams were obtained for several elements which were coated as residues on the surface of graphite electrodes, excited in an argon atmosphere, time-sectored to prevent the first 10 to 20 microseconds of radiation from reaching the spectrograph, and recorded photographically. Using time resolution, improvements in sensitivity of greater than an order of magnitude were found for cases of spark excitation where the line intensity was not easily measurable in total light exposures because of high background intensity. The studies were made using a uni-directional discharge and the traditional oscillatory discharge. Examples are given of the types of information to be derived from rotating mirror and rotating disk exposures, the advantages and disadvantages of each for testing and developing a spectrochemical procedure using spark excitation.

The author wishes to express his appreciation to Professor Gilbert H. Ayres of the University of Texas and to Dr. C. F. Metz and Dr. David W. Steinhaus of the Los Alamos Scientific Laboratory for their support and encouragement during the course of this investigation. Acknowledgment is made to the Los Alamos Scientific Laboratory for providing the funds and facilities for the research.

December, 1965 Harold Morris Burnett

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# CHAPTER I

# INTRODUCTION

## A. General

In recent years there has been an increased interest in materials in which traces of impurities are of great importance. The materials used in nuclear reactors, solid state devices, biological systems, and most recently in space applications often demand an extremely high degree of purity. The use of such materials has provided the impetus for investigations into methods to evaluate the purity of materials and to study the effects of such impurities.

The requirements for the analysis of purified materials often exceeds the capabilities of currently existing analytical techniques. This is true because special preparative methods have made it possible to produce materials where trace impurities may be a few parts per billion or even less. It is desirable that methods be developed that can combine extreme sensitivity with reasonable precision.

In all methods used for trace analysis, there is an underlying problem that requires the ability to resolve a weak signal from a background or background noise of almost equivalent magnitude. Spectro-

graphic techniques have been used widely for trace analysis and detection limits have been extended to quite low levels by improving the sources of radiation and closely controlling other instrumental factors. The ability to measure very low concentrations is improved by increasing the signal-to-noise or line-to-background ratio. One method of improving sensitivity by significantly reducing the noise or background is found in the application of time-resolved spectra, the technique used in this investigation.

B. Review of Literature

With a light source that changes rapidly with time, it is very useful to study the radiation from the source by resolving its spectrum in time. The time dependent behavior of the light results from rapidly changing parameters, such as temperature, electric current, recombination of ions and electrons, etc. Since the early investigations of Schuster and Hemsalech[1] in 1900 on the order of appearance of continuous radiation and different spectral lines in spark discharges, time-resolved spectroscopy has advanced greatly in instrumentation and application. Investigations of hot plasmas, temperatures within gaseous discharges, spark souces, intensities of individual spectrum lines and continuous radiation represent some typical applications.

A large number of investigations using time-resolved spectroscopy have been done on single high energy events, such as nuclear explosions, wire explosions, and some types of discharges. Other investigations, utilizing sources where a sufficient amount of light is not found in a

1. Schuster, A. and Hemsalech, G., Trans. Roy. Soc. (London) 193, 189 (1900).

single event for detection by the most sensitive means available, were made possible with the development of electronic techniques for synchronization and superposition of many single events. With the development of such techniques, the tool of time-resolved spectroscopy was available for analytical purposes in spectrochemistry. Most of the developments and applications for spectrochemical use date from about 1950. However, Dienum and Boer[2] in 1939 used a rotating disk for time-resolution and superposition of low energy sparks as used in spectrochemical analysis. They used a contact on the rim of the spinning disk to control the breakdown of the spark gap and to act as a shutter. The disk, which contained a single slot set at 45° to the spectrograph slit, gave a time resolution of about 20 $\mu$sec. The progress since 1950 is emphasized in the review of developments and applications presented in the next several pages.

For spectrochemical applications of time-resolved spectroscopy, the chemical concentration has to be determined from the integrated signal from a large number of individual sparks. One of the early applications of time-resolved spectroscopy to spectrochemistry was the work of Crosswhite, Steinhaus, and Dieke.[3,4] Their investigations showed that selected time intervals of the radiation from spark discharges could be used advantageously to achieve a higher line-to-background ratio than could be achieved

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2. Dienum, H. and deBoer, F., Spectrochim. Acta 2, 318 (1944).

3. Crosswhite, H. M., Steinhaus, D. W. and Dieke, G. H., J. Opt. Soc. Amer. 41, 299 (1951).

4. Steinhaus, D. W. and Crosswhite, H. M., "Methods of and Systems for Spectrochemical Analysis," U. S. Patent No. 2,744,438, May 8, 1956.

by using the total light of the discharge. The suppression of certain parts of the spark spectra was accomplished by an electronic device for rendering a phototube sensitive at prescribed but arbitrary intervals of a spark cycle. At the other times, the phototube was insensitive. The potential of this scheme for chemical analysis was demonstrated by the determination of silicon in steel. The greater sensitivity resulted from a suppression of the early light which eliminated interferences from air lines, continuous background, and some spark lines that were principally excited during the initial states of the discharge. Neutral atom lines persisted for much longer periods of time and were recommended for use as analysis lines. The utilization of the late arc-like radiation by time-resolution combined some of the advantages of the arc discharge with those of the spark discharge. A further application by the same authors[5] utilized a system whereby time resolution was achieved by gating the signal between the photomultiplier tube and a recorder. They showed that a lower concentration (greater sensitivity) could be achieved for chromium in iron by utilizing the light between 32-38 $\mu$sec. of each discharge for recording. The spectrochemical applications were not investigated extensively as their investigations were principally concerned with the time dependent behavior of line and background radiation produced in spark discharges;[6] however, the potential for utilization was clearly shown. The scheme for electronic shuttering and recording was made practical by using the breakdown of the spark as a triggering

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5. Steinhaus, D. W., Crosswhite, H. M. and Dieke, G. H., Spectrochim. Acta 5, 436 (1953).

6. Steinhaus, D. W., Crosswhite, H. M. and Dieke, G. H., J. Opt. Soc. Amer. 43, 257 (1953).

signal and averaging over many successive sparks. The shutter operating with an off-on ratio of $1:10^5$ achieved good precision for the individual lines investigated.

Bardocz and Varsanyi[7] in 1955 demonstrated that results similar to those described above could be achieved by optical means. By using a rotating mirror in connection with a high precision spark source, a single spectrum was produced on a photographic plate by superimposing several thousand discharges. The rotating mirror produced the time dispersion, and the spectrograph gave the wavelength dispersion. From the spectrograms, the time which resulted in the highest line-to-background ratio was selected. The authors illustrated the advantages of this procedure for the spectrochemical analysis of copper in aluminum. By omitting the initial stage of the discharge, an analytical curve with an improved slope was obtained for the range 0.01% - 0.2% copper in aluminum. This system required a source unit where the breakdown of the individual spark discharges had a jitter of the order of microseconds. Bardocz[8,9] has reported quite extensively on high precision electronic light sources for spectrochemical usage. In general, the breakdown of the individual discharges was achieved from an electrical pulse derived from the rotating device. Because the switching of high voltages is necessary in many applications of time-resolved spectroscopy, the subject of triggering will be

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7. Bardocz, A. and Varsanyi, F., Z. Naturforsch. 10a, 1031 (1955).

8. Bardocz, A., VII Colloquium Spectroscopicum Internationale, Sept. 1958, Rev. Universelle des Mines 15, 344 (1959).

9. Bardocz, A., Appl. Spectro. 11, 167 (1957).

discussed more fully in Chapter II.

Hagenah and Laqua[10, 11] have reported detailed time-resolved studies on the behavior of aluminum and zinc, as well as the behavior of several impurities in zinc. Their results showed that in some cases the utilization of time-resolution techniques resulted in improved sensitivity with greater precision. The improvement in line-to-background ratio was often very small when comparisons were made between time-resolved exposures and high inductance sparks which have a pronounced arclike character. The required increase in the time for each exposure in the time-resolved case was a definite disadvantage of the technique. They also studied the effects of changing current[12] on the behavior of emission lines of the electrode material and surrounding gas, and the background continuum using time-resolved spectra of aluminum and zinc. The possibilities of using time-resolved spectroscopy for routine spectrochemical analysis were investigated by these authors.[13] They reported that sensitivity limits were comparable from time-resolved low inductance sparks and total light exposures from high inductance sparks for the analysis of several metals and alloys, i.e., aluminum, zinc, and brass.

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10. Hagenah, W. D. and Laqua, K., VII Colloquium Spectroscopium Internationale, Sept. 1958, Rev. Universelle des Mines 15, 361 (1959).

11. Hagenah, W. D., ibid. 15, 369 (1959).

12. Laqua, K. and Hagenah, W. D., VIII Colloquium Spectroscopicum Internationale, Sept. 1959, Schweizerische Arbeitsgemeinschaft fur Spektralanalyse, Luzern, H. R. Sauerlander and Co., Aarau, Switzerland (1960) p. 45.

13. Laqua, K. and Hagenah, W. D., Spectrochim. Acta 18, 183 (1962).

Time-resolved studies of the copper spark method showed some improvement through time-resolution under certain conditions; however, it was also possible to achieve poorer results through time-resolution than those obtained from total light exposures because of the nature of the coated sample. These investigations were carried out in argon and air atmospheres. Laqua and Hagenah[14] have also published a critical review of the methods and results of time-resolved spectroscopy through 1962. The review presents a chronological development of the use of time-resolution techniques for many types of spectroscopic measurements including some spectrochemical applications.

Schroeder and Strasheim[15] have reported on a system of triggering which allows the details of a discharge to be studied from the onset of the discharge. This is in contrast to earlier work[16] which used the early portion of a discharge pulse to trigger the switching mechanism of the photomultiplier tube. They made detailed study of several analysis and matrix lines which are used for the analysis of copper in aluminum. They reported that alloy composition must be considered when time-resolved techniques are applied for analytical purposes because the duration of radiation of the individual lines was dependent on the composition of the

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14. Laqua, K. and Hagenah, W. D., X Colloquium Spectroscopicum Internationale, Spartan Books, Washington, D. C., 1963, p. 91.

15. Schroeder, W. W. and Strasheim, A., IX Colloquium Spectroscopicum Internationale, June 1961, Publication du Groupement pour Li Advancement des Methodes Spectrographiques (G. A. M. S.) Muray-Print, Paris (1962) p. 117.

16. Strasheim, A. and Schroeder, W. W., VII Colloquium Spectroscopicum Internationale, Sept. 1958, Rev. Universelle des Mines 15, 331 (1959).

alloy.

Majkowski and Joseph[17] have reported on the time behavior of oscillatory discharges in several different atmospheres. The effects of changing source parameters and atmospheres was shown for several atom and ion lines from a nickel alloy matrix. They reported that improved line-to-background ratios were obtained in air when the initial 10 μsec. of each discharge was not used. They found that the late stages from 50 μsec. on did not have a favorable sensitivity ratio. Additionally, they reported that the elimination of these times in other gases (nitrogen, argon, oxygen) did not improve the sensitivity. The intensity ratios calculated from comparable time intervals of the time-resolved exposures showed wide variations with alloy composition and atmosphere composition.

In addition to the studies of the high voltage spark, there have been several investigations of precisely controlled electronic arcs. The principal advantage offered is a more stable and reproducible arc with better control over the heating problems when peak amperages of up to 200 amps. are used. Strasheim[18] utilized a high voltage a. c. arc for time resolution studies. He found that little or no advantage in sensitivity was gained by using a rotating sector which subdivided the discharge into eight equal portions. This resulted from the almost simultaneous emission of arc lines, spark lines, and background during the first five-eighths of the arc cycle and the lack of any significant afterglow light. He reported that the isolation of a portion of the a. c. arc cycle could not be recommended as a

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17. Majkowski, R. F. and Joseph, B. W., Spectrochim. Acta 18, 77 (1962).

18. Strasheim, A., Appl. Spectro. 11, 76 (1957).

standard procedure because of the complexity of additional apparatus and the relatively small improvement in the line-to-background ratios for the analysis lines. However, the technique is very useful for providing information which aids in the proper selection of line pairs for the elements of interest and the internal standard. Further studies with the a.c. arc were made by Baker.[19] He used a triggered low voltage a.c. arc to study the reproducibility of time-resolved spectra of zirconium from a bismuth trioxide matrix. Using lanthanum as an internal standard, the author reported no significant difference in reproducibility between total light and time-resolved exposures. Also, the elimination of early light from the discharge offered no significant advantage because the power dissipation in the analytical gap at the beginning of the discharge is low compared to the high voltage spark discharge; and the emission of air lines, spark lines, and continuum is relatively low.

Closely associated with spectrochemical problems are investigations of the behavior of light sources and studies of the evaporation of samples from electrodes. The mechanism of spark breakdown and the behavior of the spark channel have been the subject of many investigations over the past fifty years. Very extensive investigations were made by Beams[20,21] in the 1920's on the behavior of spectrum lines in a spark discharge. He used a Kerr cell shutter in an open-closed sequence. The

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19. Baker, C. A., United Kingdom Atomic Energy Authority, Research Group, Report AERE-R 2926, 1959.

20. Beams, J. W. and Brown, J. L., J. Opt. Soc. Amer. 11, 11 (1925).

21. Beams, J. W., ibid. 13, 597 (1926).

Kerr cell was connected in parallel with the spark gap under investigation to obtain accurate synchronization. Delay lines were used to shift the open time of the shutter with respect to the firing of the spark gap. With each system, he was able to determine the behavior of emission lines in the very earliest times, the first $10^{-9}$ to $10^{-6}$ seconds. He also used a high speed rotating mirror[22] (1600 rps) to record the appearance of spectrum in the very early times. By measuring the time of appearance of spectrum lines at different places in the gap, it was possible to measure the velocities of the vapor jets. Many such measurements have been reported. The works of Kaiser,[23] Cundall,[24] and Sukhodrev[25] are examples. The velocities depended on the discharge conditions, the surrounding atmosphere, and the atomic weight of the electrode material.

In recent years, advanced electronics instrumentation has expanded the possible ways to observe time-resolved spectra. Improved photoelectric schemes,[26] image converter tubes, and other types of intensifier tubes[27] have been used.

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22. Beams, J. W., Phys. Rev. 33, 1086 (1929).

23. Kaiser, H. and Wallraff, A., Ann. d. Physik 5, 34 (1939).

24. Cundall, C. M. and Craggs, J. D., Spectrochim. Acta 7, 149 (1955).

25. Sukhodrev, N. K. and Mandelstam, S. L., Opt. i Spektroskopiya 6, 723 (1959).

26. Hovis, W. A., J. Opt. Soc. Amer. 52, 649 (1962).

27. Anan'ev, Yu. A. and Mak, A. A., Optika i Spektroskopiya (Eng. trans.) 12, 440 (1962).

C. Purpose of Investigation

The review of the literature shows that time resolution is a very useful tool for the study of spectral phenomena. The several investigations which emphasized spectrochemical applications demonstrate that time resolution can be very informative in the establishing of a spectrochemical procedure. Many variables have been investigated using several different types of discharges, but many variables remain to be investigated and others re-investigated. This investigation was initiated to study some specific applications and determine the analytical significance of several variables which are fundamental to spark discharges and are related ultimately to sensitivity.

The specific objectives were to:

1. Investigate the lowering of detection limits through the use of photographic recording of time-resolved spectra. The methods to be studied were those in which the sample is coated on the surface of electrodes, as in the so-called copper and graphite spark techniques, and those that use metal electrodes. A goal of an improvement of an order of magnitude over total light methods of spectrographic analysis was established as one in which there would be considerable interest for spectrochemists.

2. Correlate certain fundamental aspects of the various techniques of spectrochemical analysis using time-resolution as the basis for correlations. The vaporization behavior of the sample material from electrodes, the distribution and change of intensity with time and space in the analytical gap, and the effect of the different dis-

charge atmospheres were of special interest.

Line-to-background intensity ratios provide the basis for comparing different parameters and evaluating the effects of time resolution. Time resolution was to be accomplished by using a rotating mirror or disk.

# CHAPTER II

# EXPERIMENTAL

## A. Introduction

Many ways to achieve time-resolution were indicated in the previous chapter. These may be grouped as mechanical or inertial devices, electro-optical, magneto-optical, or electronic as well as combinations of these. Each has definite limits in performance with respect to time-resolution and some have limitations in wavelength coverage. A comparison of performance data for the different devices used in time-resolved spectroscopy has been compiled from the literature by Laqua and Hagenah.[1] For this investigation, the choice of inertial devices for time-resolution with photographic recording was made. Primary emphasis was placed on a unidirectional type of discharge. Based on these choices, the necessary instrumentation and conditions to electronically control the source and achieve time-resolution through the use of rotating devices were established.

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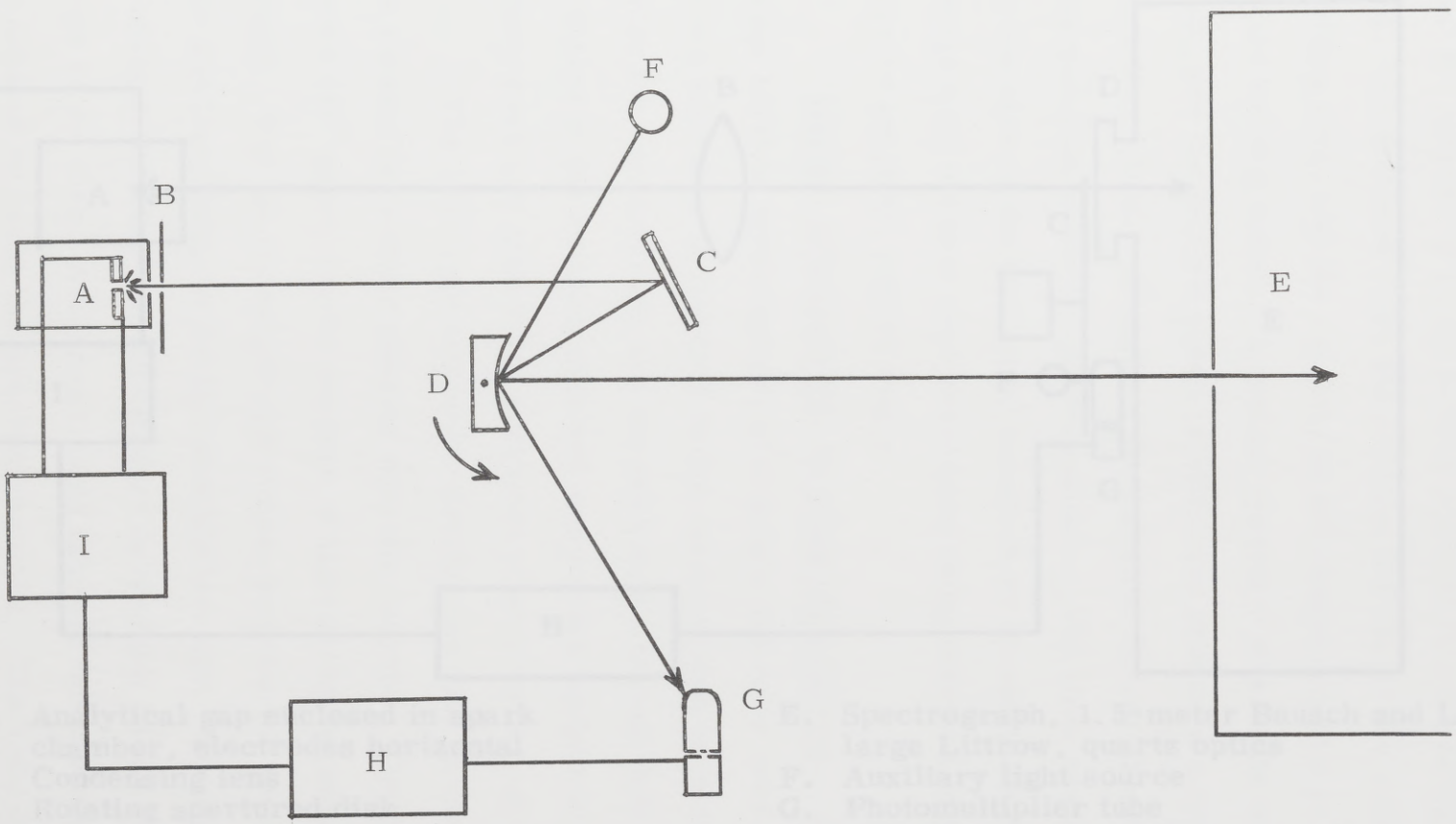
1. Laqua, K. and Hagenah, W. D., X Colloquium Spectroscopicum Internationale, Spartan Books, Washington, D. C., 1963, p. 104.

B. Time and Spectral-Resolving Systems

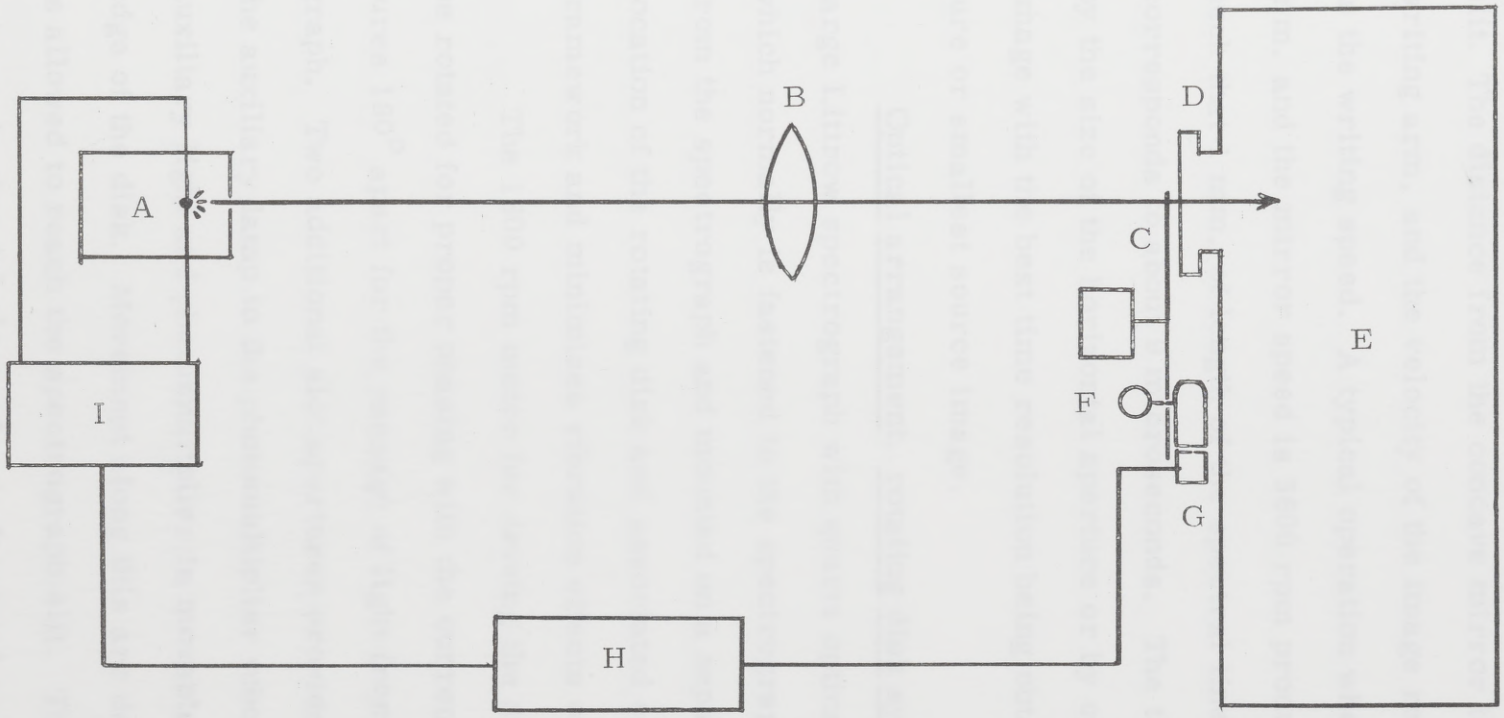
The systems for achieving time and spectral resolution used in this investigation are shown schematically in Figures 1 and 2. Although both systems utilize a rotating device for achieving time-resolution, the information derived is different, and each has certain advantages in operation and the use that can be made of the data obtained. The general aspects of optical arrangement are given here, and the specific methods for carrying out the experiments are given in a later section.

Optical arrangement, rotating mirror system. A Baird 3-meter concave grating spectrograph is used. The four inch, 15,000 groove per inch grating gives a first order dispersion of 5.7 A. $mm.^{-1}$. For time-resolution, it is required that a point image be produced at the plate which can then be dispersed in time and wavelength in two directions at right angles. Although there is inherent astigmatism with the concave grating, it is possible to produce the stigmatic spectra required for time-resolution by using a crossed slit system. One horizontal slit is placed near the source (electrodes vertical), and the concave rotating mirror is placed so that the light passed by this horizontal slit is focussed at the stigmatic focus point of the spectrograph. The horizontal slit near the source provides the ability to make spatial studies within the gap. The distances between the source and rotating mirror are adjusted so that there is a 3:1 reduction at the stigmatic focus of the area defined by the horizontal slit. The spectrograph slit is 25 or 50 microns wide. The rotating mirror, driven by 3600 rpm synchronous motor, sweeps the source image along the plane parallel to the slit. This is comparable to imaging the source on the slit of a stigmatic spectrograph and sweeping the image along the length of




A. Analytical gap enclosed in spark chamber - electrodes vertical
B. Horizontal slit
C. Folding mirror
D. Rotating mirror
E. Spectrograph, Baird 3-meter Eagle mounting
F. Auxiliary light source
G. Photomultiplier tube
H. Trigger pulse generator
I. Power supply; spark source with controlled switch

Figure 1. Rotating mirror system for obtaining time-resolved spectra




A. Analytical gap enclosed in spark chamber, electrodes horizontal
B. Condensing lens
C. Rotating apertured disk
D. Spectrograph slit
E. Spectrograph, 1.5-meter Bausch and Lomb, large Littrow, quartz optics
F. Auxiliary light source
G. Photomultiplier tube
H. Trigger pulse generator
I. Power supply; spark source with controlled switch

Figure 2. Rotating disk system for obtaining time-sectored spectra

the slit. The rotating mirror is synchronized with the optical source so that the mirror is in the proper position to scan along the length of the slit. The distance from the concave mirror to the point of focus is the writing arm, and the velocity of the image relative to the slit (or film) is the writing speed. A typical operation where the writing arm is 300 mm. and the mirror speed is 3600 rpm produces a time dispersed spectrum such that 1 mm. of length of the spectral line at the photographic plate corresponds to about 9 microseconds. The time resolution is controlled by the size of the horizontal aperture or by optically reducing the source image with the best time resolution being obtained with the smallest aperture or smallest source image.

Optical arrangement, rotating disk system. A Bausch and Lomb large Littrow spectrograph with quartz optics is used. The optical bench which normally is fastened to the spectrograph is moved about 5 inches from the spectrograph and mounted on a separate table. This permits the location of the rotating disk and associated equipment on the optical bench framework and minimizes vibration effects on the spectrograph.

The 1800 rpm motor for driving the disk is mounted so that it may be rotated for proper phasing with the current. The disk has two apertures $180^{\circ}$ apart for the passage of light from the source to the spectrograph. Two additional slot apertures provide for the passage of light from the auxiliary lamp to the photomultiplier tube. The plate containing the auxiliary light and photomultiplier is movable along an arc parallel to the edge of the disk. Movement along this arc determines the time that light is allowed to reach the spectrograph slit. The light from the discharge between horizontal electrodes is focussed on the vertical entrance slit of

the spectrograph. A quartz cylindrical lens is used at a position so that the light entering the spectrograph originates from a constant interval between the electrodes. The interval has a width equal to the slit width. Part of the disk system is shown in Figure 3.

C. Precision Control of Initiation of Spark Discharge

To use rotating devices successfully for time resolution, there is the requirement for a high degree of precision in the initiation of the spark discharge. This precision control involves the problems of switching relatively high voltages and methods for triggering the source at the proper time so that there is a proper relationship between the angular position of the rotating devices and the time of initiation of the spark discharge in the analytical gap.

In present day spectrochemical practice, the air-interrupted gap high-voltage spark source is used almost exclusively. The control of the breakdown of the spark discharge by this means, or through rotary gap control, results in a breakdown of successive discharges which may vary as much as ±50 microseconds in relation to the phase of the input current. For time-resolved studies of phenomena which are of 10-100 microseconds duration, it is evident that such control is not adequate if the time resolving devices are of the inertial type. The problems associated with the switching of high voltages with high precision have been investigated quite thoroughly in recent years and several means for accomplishing the switching have been developed. Malpica and Berry[2] used an ignitron as a controlling element for voltages and currents comparable to those found

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2. Malpica, J. T. M. and Berry, T. M., Gen. Elec. Rev. 44, 563 (1951).

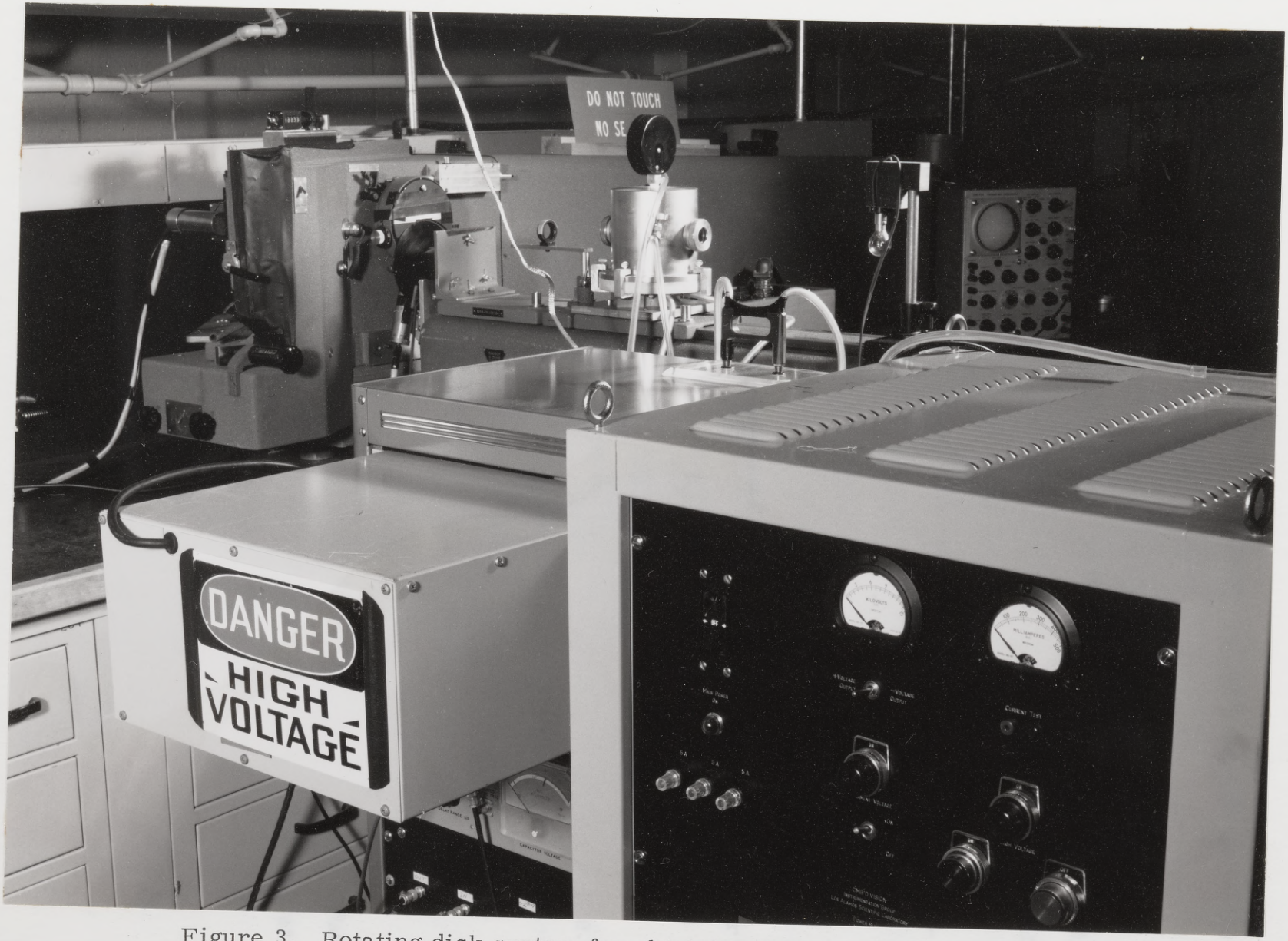


Figure 3. Rotating disk system for obtaining time-resolved spectra

in standard spectroscopic practice. Ignitrons are also used in capacitor discharge circuits operating up to 20,000 volts at peak currents of $10^5$ amperes. These very high currents are of special interest for the production of very highly ionized spectra. Thyratron tubes are widely used. Present day tubes can switch voltages as high as 40,000 volts at repetition rates greater than 2000 per second and with pulse currents as high as 3000 amperes. These ratings are well above the requirements for spectrochemical usage where one is primarily interested in spectrum lines produced from the excitation of the neutral atom or singly ionized atom, first or second spectrum. Bardocz[3,4] has described extensively the principles and advantages of using a thyratron-spark gap combination for the control of spectrographic spark sources.

Several types of switching devices were tested for use in this investigation. These included ignitron, thyratrons and an optical linkage. An ignitron switch was operated satisfactorily at discharge rates up to 15 per second with an observed scatter of 0.2 $\mu$sec. in an electrical signal derived from the discharge. Because it was desirable to operate at higher discharge rates than was possible with the particular ignitron switch arrangement tested, further tests of ignitrons were not made. The thyratron triggered supply was tested over a wide range of voltages and at repetition rates up to 60 per second. The optical system tested was an

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3. Bardocz, A., Nature 171, 1156 (1953).

4. Bardocz, A., Spectrochim. Acta 7, 307 (1955).

arrangement similar to that of Schroeder and Strasheim.[5] This system utilizes two independent spark sources except for the optical linkage for breakdown of the discharge. One source is a conventional auxiliary air gap spark source adjusted so that the voltage is just below the breakdown voltage for a given auxiliary gap spacing. The second source is a precisely triggered low power source for control of the breakdown time. The spark gap of the second source is placed adjacent to the auxiliary gap of the first source. The gap for the triggered source is a sliding type spark utilizing an open end of coaxial cable and a grooved lavite spacer as the insulator. In operation, the radiation from the gap of the triggered source produces free electrons in the auxiliary gap and facilitates the breakdown of the gap. The optical linkage provides for an instantaneous breakdown of the analytical gap. This system is used for producing an oscillatory type discharge for time resolution studies. This type of triggering system has advantages in that an unlimited range of voltages and currents can be triggered without using gas tubes. It should be emphasized that such a spark gap system is bidirectional in current conduction while those using gas filled or vacuum tubes are usually unidirectional.

The hydrogen thyratron switching system tested was selected as the major switching device for this investigation. The spark circuit with the incorporated thyratron used is shown in Figure 4. The thyratron, an Amperex 6279, is capable of operating up to 16 kv. with peak currents of 325 amperes. During the charging cycle, the thyratron is an open switch

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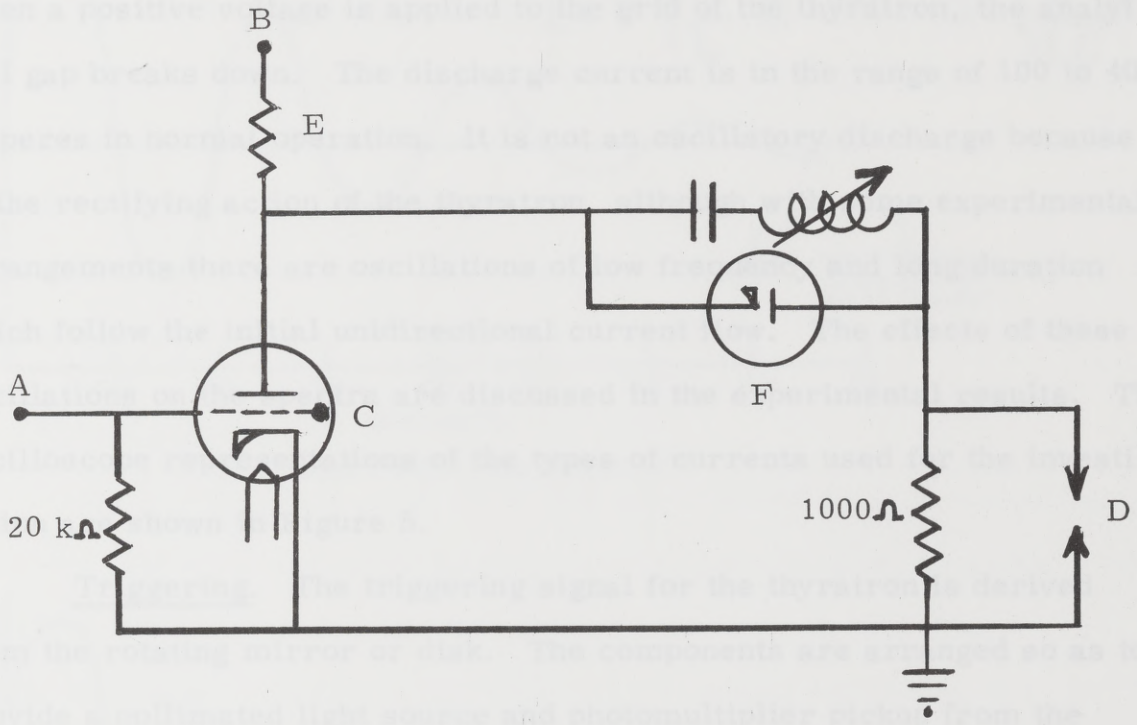
5. Schroeder, W. W. and Strasheim, A., IX Colloquium Spectroscopicum Internationale, June 1961, Lyon, France, Muray-Print, Paris, 1962, p. 117.




A. Trigger pulse input

B. High voltage d.c. power supply

C. Hydrogen thyratron, Amperex 6279

D. Analytical gap enclosed in spark chamber

E. Charging resistor (or inductor)

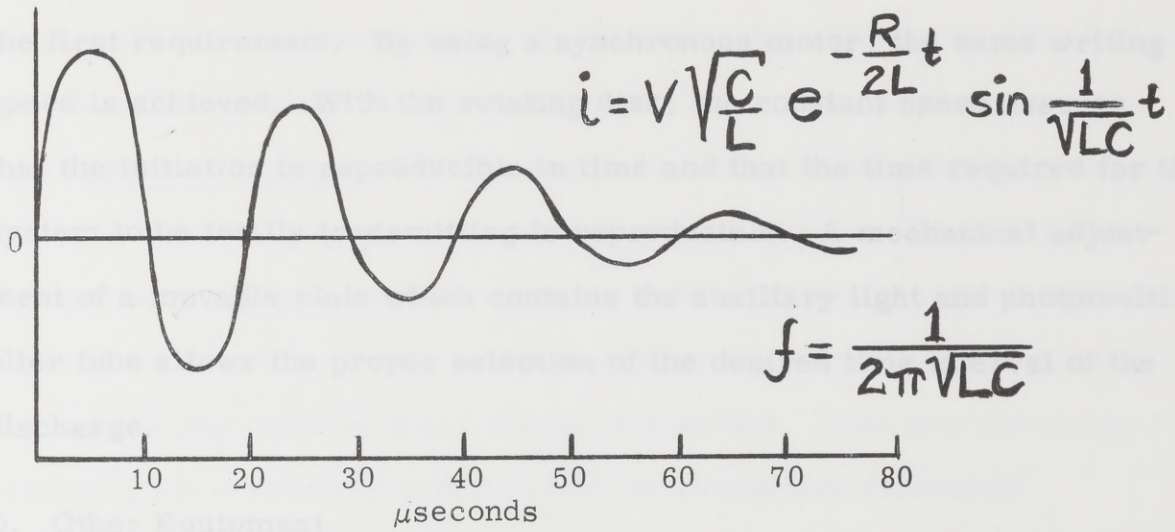
F. Rectifier tube, RCA 8020

Capacitance, 0.075 $\mu$F; Variable inductance, residual to 600 $\mu$H

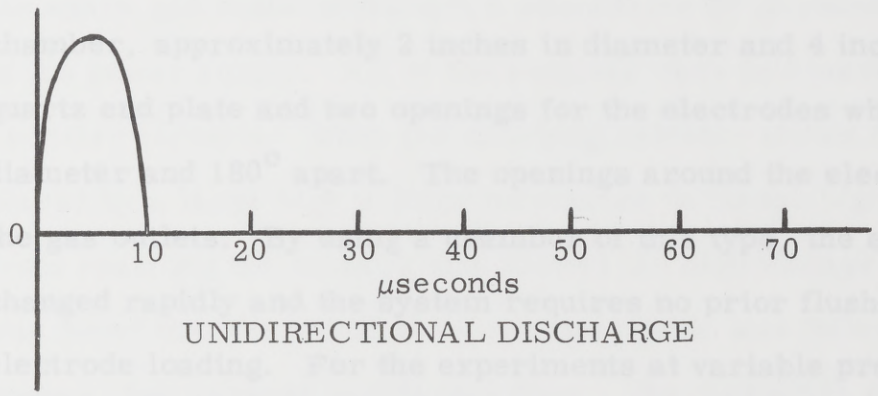
Figure 4. Spark discharge switching circuit using a hydrogen thyratron.

and is effectively removed from the circuit while the capacitor charges. When a positive voltage is applied to the grid of the thyratron, the analytical gap breaks down. The discharge current is in the range of 100 to 400 amperes in normal operation. It is not an oscillatory discharge because of the rectifying action of the thyratron, although with some experimental arrangements there are oscillations of low frequency and long duration which follow the initial unidirectional current flow. The effects of these oscillations on the spectra are discussed in the experimental results. The oscilloscope representations of the types of currents used for the investigation are shown in Figure 5.

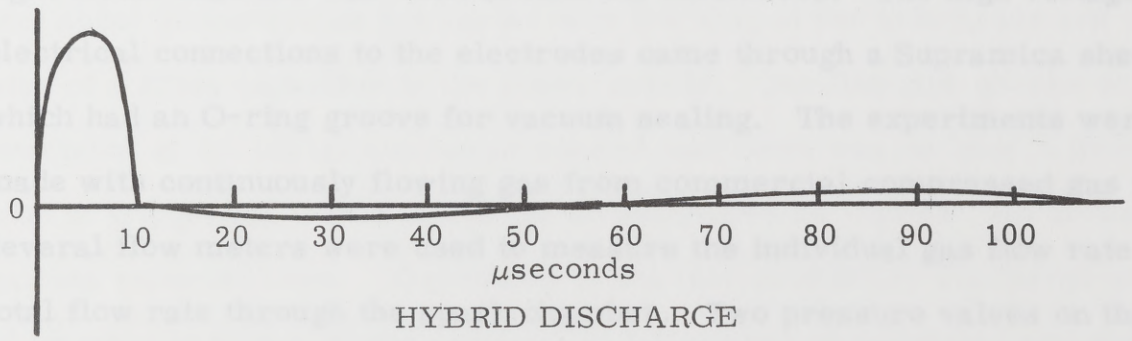
Triggering. The triggering signal for the thyratron is derived from the rotating mirror or disk. The components are arranged so as to provide a collimated light source and photomultiplier pickup from the rotating mirror or from a slot in the disk. The light source is a tungsten line filament lamp operated by a well stabilized d. c. supply at about 8 volts. A 931A photomultiplier tube with the necessary resistors and capacitors built into a single enclosed unit to minimize the pickup of stray signals was the detector for the auxiliary light. When a positive pulse from the photomultiplier was required, the signal was taken from the ninth dynode of the 931A tube. For the superposition of many individual events with a rotating mirror, it is required that the discharge be initiated when the mirror is in a given position in space and when it is rotating at a constant speed. The first requirement insures that every streak starts at the same point while the second insures that the superimposed records have the same writing speed. Through the positioning of the auxiliary light, the photomultiplier tube, and the rotation of the motor it is possible to meet




OSCILLATORY DISCHARGE




UNIDIRECTIONAL DISCHARGE




HYBRID DISCHARGE

Figure 5. Types of discharge current; simplified equations showing variables determining the current i. V, voltage; C, capacitance; L, inductance; f, frequency.

the first requirement. By using a synchronous motor, the same writing speed is achieved. With the rotating disk, the constant speed assures that the initiation is reproducible in time and that the time required for the system to be totally transmitting is reproducible. A mechanical adjustment of a movable plate which contains the auxiliary light and photomultiplier tube allows the proper selection of the desired time interval of the discharge.

D. Other Equipment

Spark Chambers. For all of the experiments done at atmospheric pressure (approximately 580 torr), a pyrex glass chamber was used. The chamber, approximately 2 inches in diameter and 4 inches long, has a quartz end plate and two openings for the electrodes which are 3/8" in diameter and 180° apart. The openings around the electrodes served as the gas outlets. By using a chamber of this type, the electrodes can be changed rapidly and the system requires no prior flushing for each new electrode loading. For the experiments at variable pressures, a vacuum tight metal chamber was built around the electrodes. The high voltage electrical connections to the electrodes came through a Supramica sheet which had an O-ring groove for vacuum sealing. The experiments were made with continuously flowing gas from commercial compressed gas tanks. Several flow meters were used to measure the individual gas flow rate or total flow rate through the spark chamber. Two pressure valves on the chamber permitted the adjustment of the pressure and flow rate. A conventional vacuum pump was attached to one outlet for reducing the pressure below atmospheric. The pressure was measured with a compound gauge which was calibrated with a mercury manometer. A flow rate of 4 liters

per minute was used for most of the experiments. The metal chamber and associated equipment are shown in Figure 3.

Power Supplies. For the production of an oscillatory discharge, a conventional auxiliary air gap spark source was used. The principles of the operation are well known and documented.[6] A few minor changes were made in the primary circuit of the transformer so that the voltage for breakdown of the gap could be more closely controlled. This was necessary for producing time-resolved exposures of the oscillatory discharge.

Several d.c. power supplies were built for use with the spark circuit shown in Figure 4. The requirement for increasing power within the spark gap made necessary a succession of increases in the capabilities of the power supply. All of the supplies were full-wave center-tapped rectifier circuits. When the charging resistor shown in Figure 4 was replaced by a large high voltage inductance to hinder high frequency currents from reaching the network and protect the high voltage rectifier tubes, it was found that the initial unidirectional pulse was followed by a low frequency, low current oscillatory flow. The frequency of this oscillatory flow was about 20 kilocycles but varied with the size of the inductance and the size of a filter capacitor in the power supply. Oscilloscope checks on the precision of the initial discharge showed that there was no loss in precision of triggering. This discharge is designated as "hybrid" for investigations reported here. The effects of the late oscillatory discharge were of interest in terms of any increase in the amount of excitation and possible

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6. Enns, J. H. and Wolfe, R. A., J. Opt. Soc. Am. 39, 298, (1949).

improvement in line-to-background ratio. With the filter capacitor removed, the current flow was purely unidirectional. The duration of the unidirectional flow was varied by changing the inductance in the discharge circuit. With the change in the time of current flow, there was also a change in the peak current.

E. Experimental Procedure

For practical spectrochemical usage, it is necessary that there be a means of making many separate exposures in a reasonable length of time once the conditions for exposure have been determined. This is especially true with coated graphite electrodes where a long delay between electrode preparation and time of excitation can produce deleterious results. For this investigation, there was no attempt made to optimize this factor; however, it is felt that the solution is principally one of engineering and can be optimized satisfactorily. The spark chambers used introduced no large time factor for the changing of electrodes.

Rotating Mirror System. Before the preparation of samples, it was necessary to check the optical system and other components. The rotating mirror system was adjusted for proper phasing of the mirror and discharge by viewing the grating illumination from the focal curve of the spectrograph. With the excitation parameters set and the optical arrangement checked, samples were prepared and the exposures made for the gap spacing and region of the gap desired.

Rotating Disk System. With the rotating disk, the arbitrary microsecond time interval at which the light is allowed to reach the spectrograph must be set. For the investigations reported here, this time was designated as the "on-time", or $t_1$. Figure 6 shows pictorially the oscilloscope

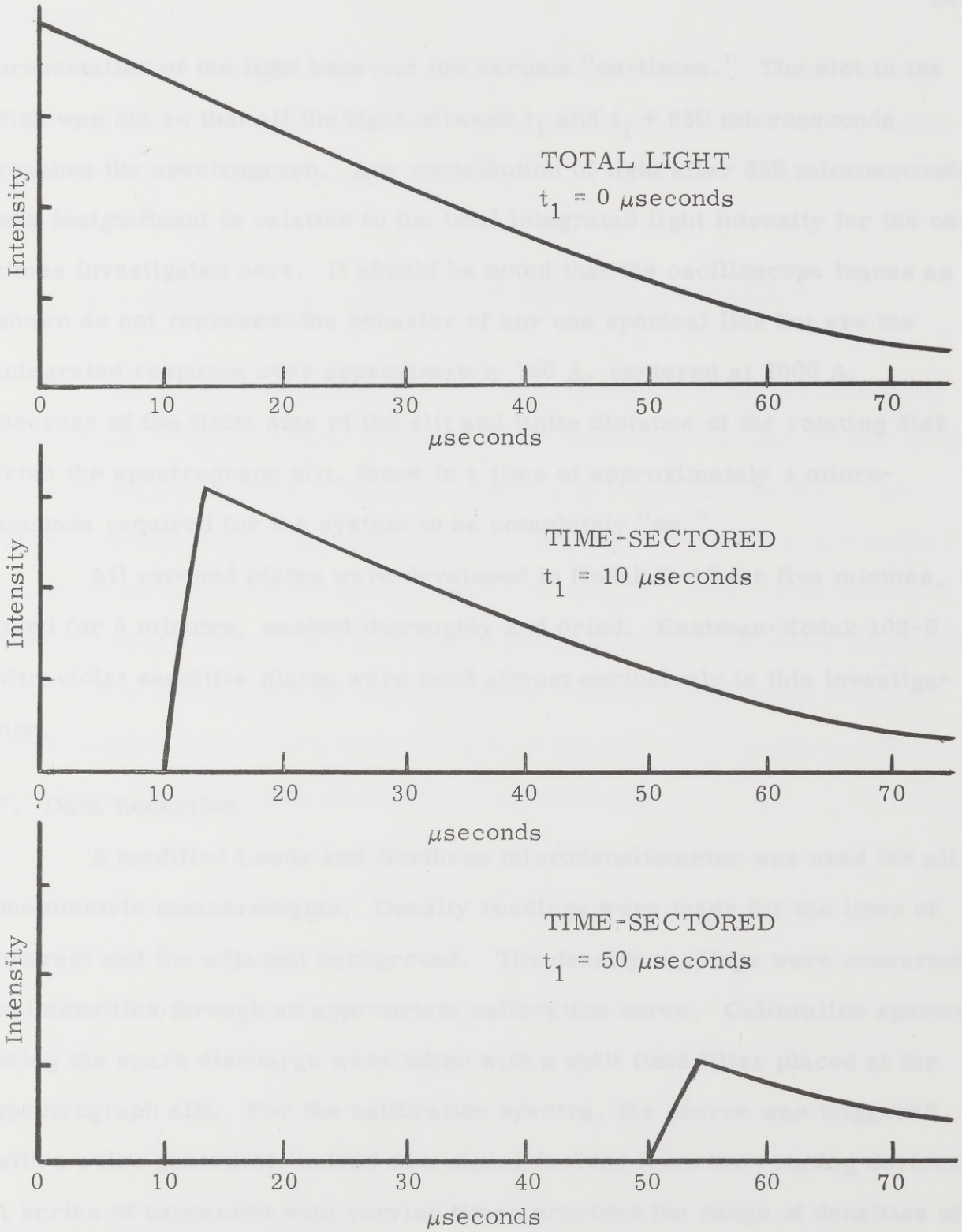


Figure 6. Use of variable on-time ($t_1$) for time-sectored exposures. Shutter open for $t_1$ + 650 μseconds.

presentation of the light behavior for various "on-times." The slot in the disk was cut so that all the light between $t_1$ and $t_1$ + 650 microseconds reaches the spectrograph. Any contribution of light after 650 microseconds was insignificant in relation to the total integrated light intensity for the on-times investigated here. It should be noted that the oscilloscope traces as shown do not represent the behavior of any one spectral line but are the integrated response over approximately 150 A. centered at 3000 A. Because of the finite size of the slit and finite distance of the rotating disk from the spectrograph slit, there is a time of approximately 4 microseconds required for the system to be completely "on."

All exposed plates were developed in Kodak D-19 for five minutes, fixed for 5 minutes, washed thoroughly and dried. Eastman-Kodak 103-0 ultraviolet sensitive plates were used almost exclusively in this investigation.

F. Data Reduction

A modified Leeds and Northrup microdensitometer was used for all photometric measurements. Density readings were made for the lines of interest and the adjacent background. The density readings were converted to intensities through an appropriate calibration curve. Calibration spectra using the spark discharge were taken with a split field filter placed at the spectrograph slit. For the calibration spectra, the source was triggered with a pulse generator instead of a signal derived from the rotating devices. A series of exposures with varying times provided the range of densities of interest. With the known transmission ratio through the two steps of the filter, the emulsion was calibrated using the two-step preliminary curve

method.[7]

For the comparison of various experimental parameters for total light and time-resolved exposures, the line-to-background intensity ratios were used. The intensity ratio, designated L/B, was calculated as follows:

$$L/B = \frac{I \text{ line}}{I \text{ background}} = \frac{I \text{ (line + background)} - I \text{ background}}{I \text{ background}}$$

The graphs are presented as smooth curves through the individual data points. The L/B ratio for each set of conditions was determined from three to ten evaluations of the photographically recorded spectra. For repetitive evaluations, the precision was determined to be ± 10% relative standard deviation for the background at values just above the threshold of the calibration curve. The L/B ratios are generally of the same precision.

For the rotating mirror exposures, micro-densitometer readings were taken at 5 $\mu$sec. intervals along the time axis of the spectra. Background corrections were made where possible.

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7. "Methods of Emission Spectrochemical Analysis", ASTM Publication, Philadelphia, Penna., 1964, p. 75.

# CHAPTER III

## EXPERIMENTAL RESULTS

### A. Introduction

Time-resolved spectra are used as a basis of correlation for several parameters which are known to effect the behavior of spark discharges and their use in spectrochemical applications. Primary emphasis is placed on the graphite spark technique and applications which utilize metal pins or rods as the electrodes. The graphite spark technique is one of several commonly used spectrochemical methods where the sample is the residue remaining after evaporating a sample solution onto an electrode. Time-resolved spectrograms using a rotating mirror system are used principally for qualitative evaluation of the effects produced by changing several variables. Spectrograms taken with a rotating disk system are used to determine the effects of time resolution on elemental line intensities, background intensities, and the corresponding line-to-background intensity ratio. Total light exposures are also made for comparison with the time-resolved exposures. This procedure provides a means for comparing the relative behavior for the

total light and time-resolved exposures by measurement of the line-to-background intensity ratios in each case.

B. Solution Residue Methods of Analysis

Probably the best known method for the analysis of very small samples is one described by Fred, Nachtrieb, and Tomkins.[1] They evaporated 0.1 ml. of a hydrochloric acid solution of the sample on the ends of 1/4-inch high purity copper electrodes and excited the sample with a high inductance spark discharge. The method has high absolute sensitivities ranging from $10^{-10}$ to $10^{-6}$ grams for the sixty-four elements tested. The method has been used extensively for radioactive materials where special handling techniques are required and the sample is often limited in size. The high absolute sensitivity coupled with separation and concentration schemes has made the technique competitive in terms of concentrational sensitivity.[2] The use of copper electrodes is limited to reagents that do not attack the electrodes. Special machining of the copper electrodes just prior to their use is also required.

Graphite has also been used for the supporting electrode in solution residue methods. The commonly used forms are 1/4-inch rods and larger platrodes, usually a 1/2-inch diameter disk which holds about 0.5 ml. of solution. Although the graphite is quite porous, there have been reports of improved sensitivity using the graphite electrodes. Morris and Pink[3]

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1. Fred, M., Nachtrieb, N. H. and Tomkins, F. S., J. Opt. Soc. Amer. 37, 279 (1947).

2. Brody, J. K., Faris, J. P. and Buchanan, R. F., Anal. Chem. 30, 1909 (1958).

3. Morris, J. M. and Pink, F. X., ASTM Spec. Tech. Pub. No. 221, 1957, pp. 39-46.

showed very good sensitivities for several elements by drying aqueous solutions onto graphite electrodes which had been previously coated with a 0.5% solution of Apiezon N grease in ether. Owens[4] combined the principles of solvent extraction with the spectrochemical method of Morris and Pink to determine as little as 10 parts per billion for impurities in high purity gallium. Grant[5] has investigated several factors in the solution residue methods applied to the analysis of agricultural and biological materials. He studied the effectiveness of several acid-proofing agents for retaining samples on the surface of graphite electrodes and the use of spectroscopic buffers. He showed that several acids in concentrations greater than 0.2 M produced regressive effects on spectral line intensities when residues were dried on graphite electrodes coated with paraffin or Apeizon N; however, the effects were not observed in hydrochloric acid solutions up to 2 M. Baer and Hodge[6] also compared five commonly used methods of spectrochemical analysis which included two methods using residues on rotating platforms and flat top electrodes. Sensitivities were compared for several acids at concentrations up to 10% v/v with the five methods. They showed pronounced line regression effects with all acids tested except hydrochloric.

In this investigation, time resolution was used to study the possibility for further improvement of the technique. Several aspects of the method

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4. Owens, E. B., Appl. Spectroscopy 13, 105 (1959).

5. Grant, C. L., Dissertation, Rutgers University, University Microfilms Mic. 60-4233 (1960).

6. Baer, W. K. and Hodge, E. S., Appl. Spectroscopy 14, 141 (1960).

were investigated. Of particular interest was the use of various atmospheres to minimize cyanogen interference and determine the effects of the atmosphere on sensitivity.

Qualitative Observations. Enlargements from portions of several spectrograms taken with the rotating mirror system are shown to illustrate the usefulness of time-resolved exposures.

The choice of a unidirectional type of discharge for this investigation necessitated some study of the vaporization and excitation behavior of materials from electrodes. Although it was recognized that a much lower amount of energy would be deposited in the analytical gap for a given power input with the unidirectional discharge as compared to an oscillatory discharge, the choice of a unidirectional discharge was made because of greater simplicity in interpreting physical and chemical phenomena which occur in the gap. With the unidirectional discharge, the vaporization and excitation arising at a particular electrode can be followed. Early experiments on volatilization and excitation behavior were made using power supplies of small power rating, 0.15 and 0.45 KVA respectively. The tests with the smaller supplies and capacitor sizes that would permit a discharge rate of 60 per second showed that satisfactory time-resolved spectra could be obtained for elements in solid electrodes; however, no satisfactory exposures could be obtained from samples coated on electrodes. The inefficiency of the volatilization and excitation was attributed to the small amount of energy in each discharge. With a larger 7.5 KVA power supply, the energy per discharge could be increased considerably by increasing the capacitance and the operating voltage. Time-resolved spectrograms which show qualitative information relative to varying source parameters, elec-

trode materials, and gaseous atmospheres are shown in Figures 7 through 10. For these exposures, the optics are arranged such that a 1 mm. horizontal screening slit produced an image with 3:1 reduction at the stigmatic point of the spectrograph. The analytical gap was 3 mm. with the slit positioned so that light was sampled near the cathode in all cases. For spectra from sample coated electrodes, a solution containing 100 $\mu$g./ml. of several elements was dried on the end of 1/4-inch electrodes (copper or graphite). The amount of solution taken for evaporation on a single electrode was 100 $\mu$l. Figure 7 shows comparative spectra as power input was increased by increasing the capacitance only. The changes do not result from a simple linear increase in the capacitance because of the corresponding changes in current and frequency which result from the change in capacitance. By comparing the spectra, it is seen that the sample spectra are more intense when the samples are coated on graphite electrodes. This is evident in both the early and late light. The spectra from the graphite electrodes clearly show the cyanogen spectra. The strong formation of the cyanogen illustrates one of the disadvantages of the graphite spark technique; namely, the interference of the cyanogen bands in the region 3500 - 4300 A. This disadvantage can be eliminated by using controlled atmospheres, in this case one that is free of nitrogen. Figure 8 shows the elimination of the cyanogen interference by using atmospheres of argon and oxygen. It is also clear from the rotating mirror pictures that elemental line histories are quite different in the different atmospheres. The background intensities are also very different. Details of the use of controlled atmospheres and their potential advantages in time-resolution are given later in this chapter. Figure 9

shows comparative spectra where inductance is the variable parameter. The spectra were taken in an argon atmosphere. Over the range of inductance values shown here, there does not appear to be any great difference in the time history of the late light. However, there are large differences in the intensity of the continuous background which markedly change the line-to-background intensity ratios for total light exposures. These observations and quantitative evaluations taken from rotating disk measurements with changing source parameters and gaseous atmospheres show that conditions which give the most favorable line-to-background ratio for total light exposures may not be the most favorable for time-resolved exposures. If one optimizes the conditions for a total light exposure and then uses time-resolved exposures for comparison, an approximate evaluation of the improvement (or lack of improvement) in sensitivity can be made. In cases where there is an improvement in sensitivity, it may be possible to extend this improvement further by optimizing all parameters relative to the time-resolved exposures. Because the detection limit of an analytical method depends on the line-to-background ratio, the change of this quantity with changes in source parameters, atmosphere, and time is of paramount importance in establishing a method. Studies of the line-to-background ratio over a wider range of inductance values were made with the rotating disk system. Figure 10 is included for comparison with Figure 7. Six exposures are comparable except for a change in the gaseous atmosphere.

Some observations concerning the features of time-resolved exposures from the rotating mirror exposures are discussed here along with indications of how they may be used advantageously for spectrochemical applications, as well as for other types of application.

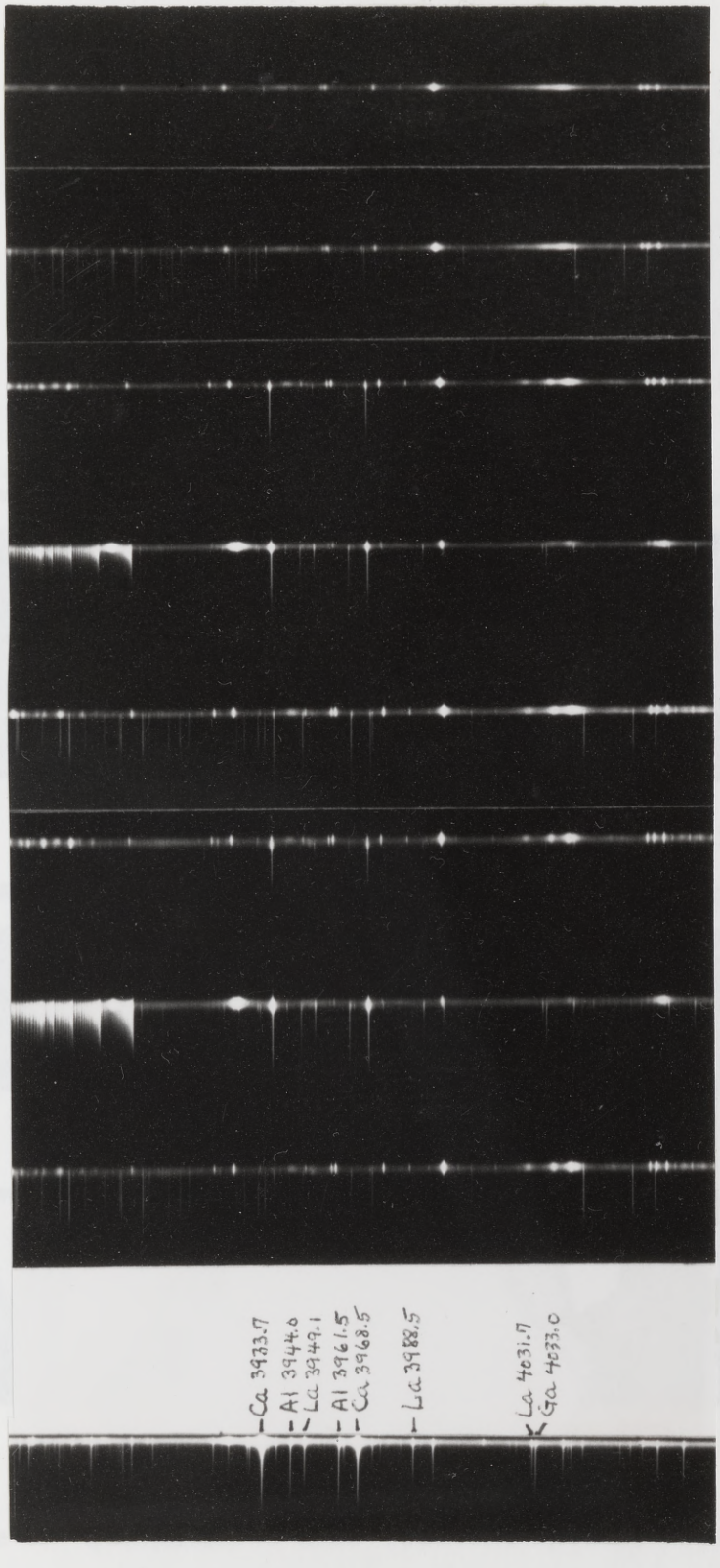


Figure 7. Comparative time-resolved spectra for variable source and excitation parameters; air atmosphere.

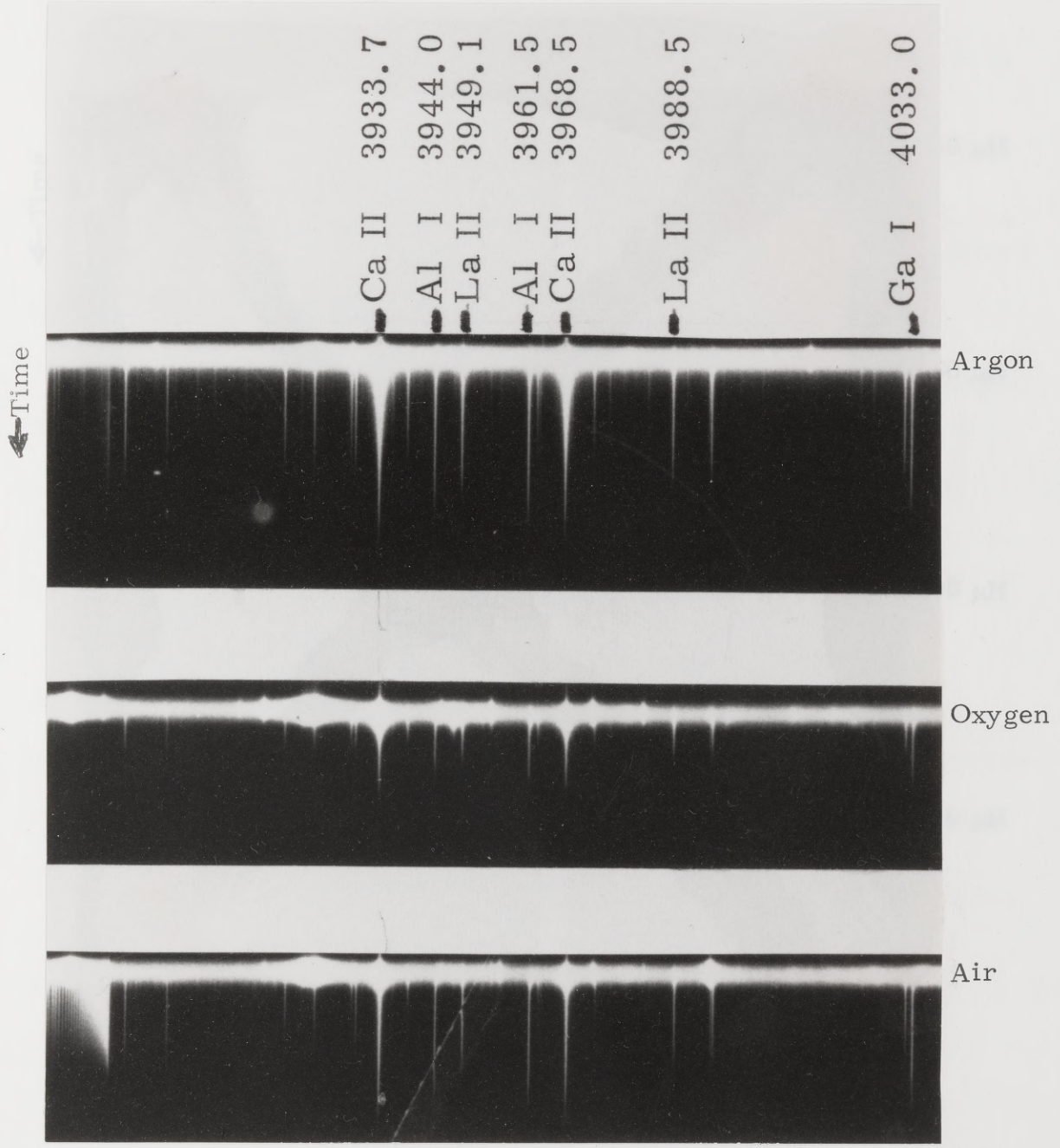


Figure 8. Comparative time-resolved spectra with controlled atmosphere excitation; sample coated on graphite electrode.

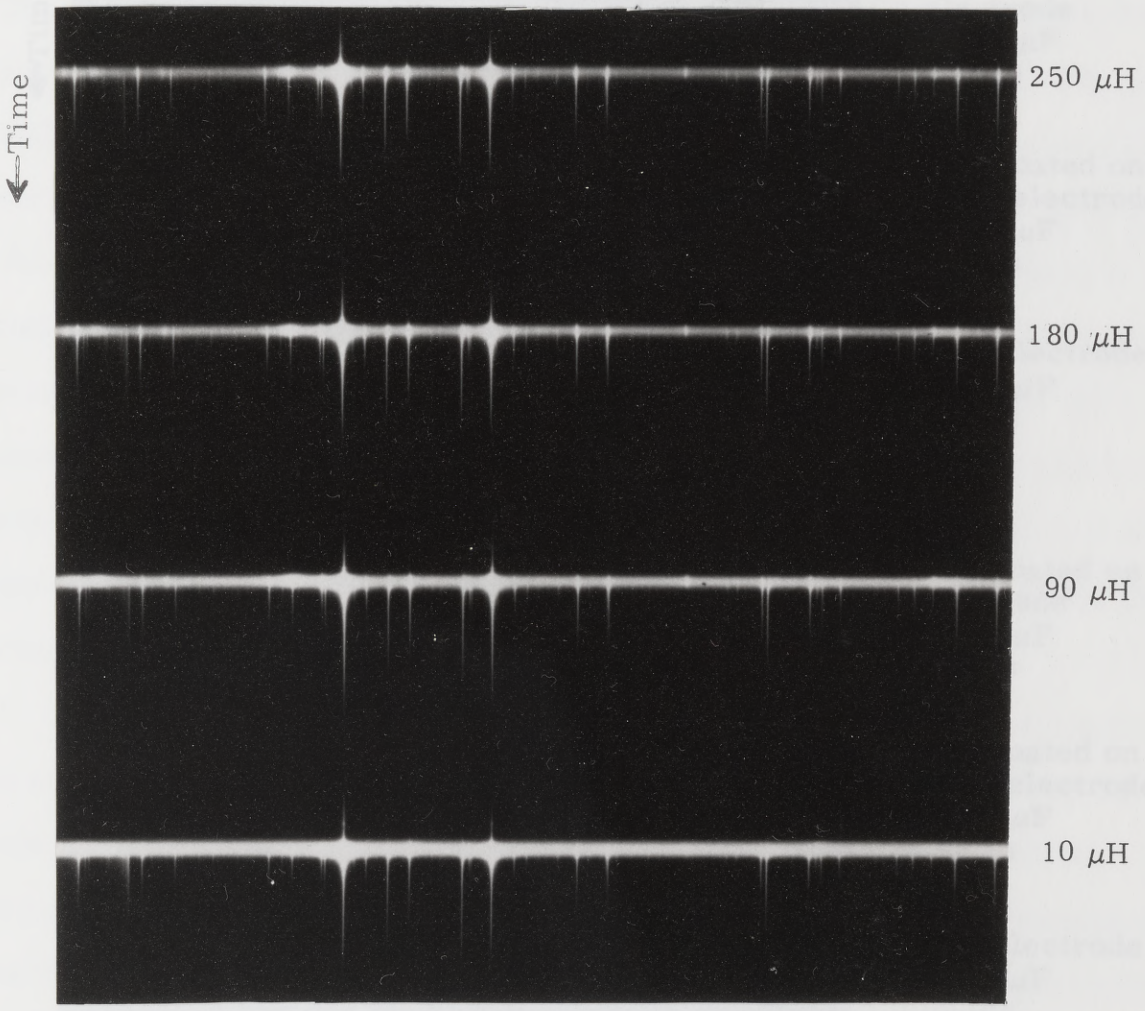


Figure 9. Comparative time-resolved spectra with variable inductance; sample coated on graphite electrode; argon atmosphere.

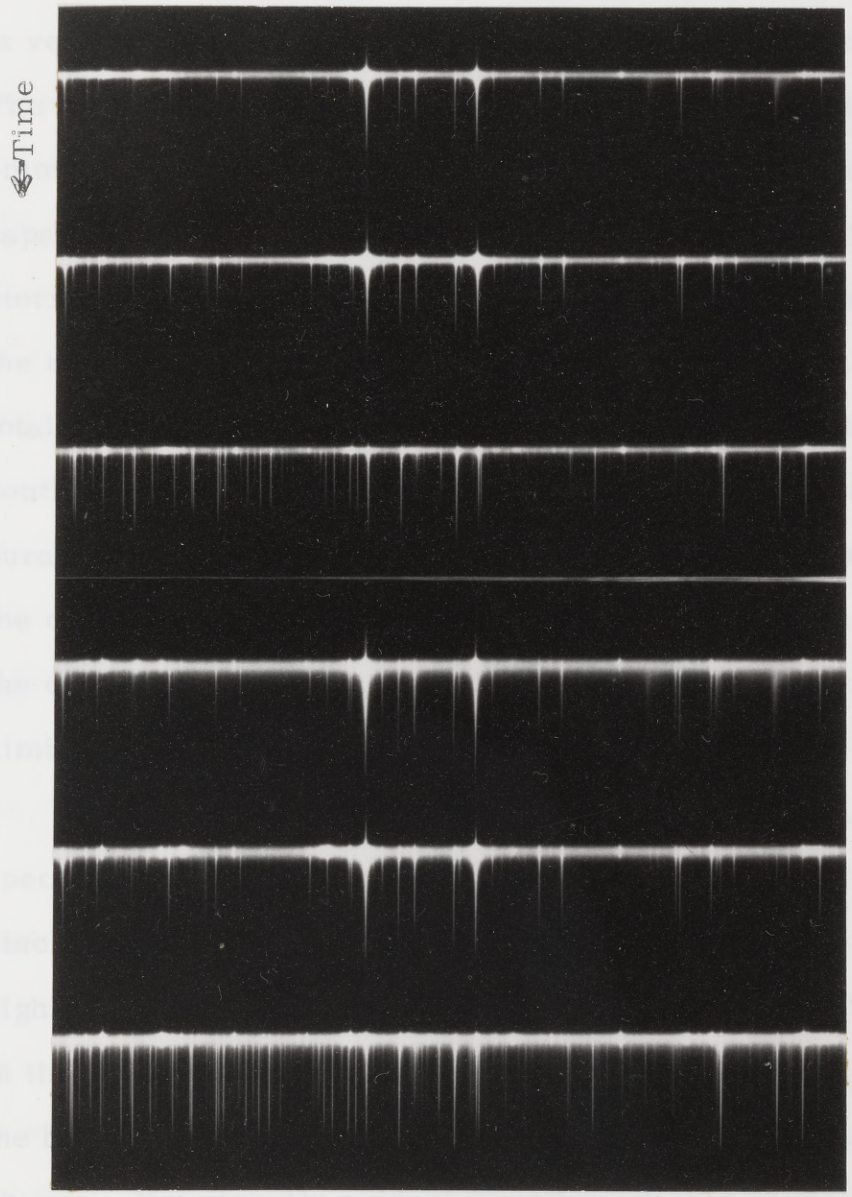


Figure 10. Comparative time-resolved spectra for variable source and excitation parameters; argon atmosphere.

1) Appearance of continuum - With the exposures taken with the uni-directional discharge and conditions described above, the continuum is very pronounced at the beginning of each time-resolved spark spectrum. The continuum is more intense and its duration is longer the greater the amount of energy input. The total light output increases as the voltage and capacitance increase and the inductance decreases. Because these parameters along with the resistance of the circuit determine the peak current, the total light output closely follows the peak current. An increase in the total light with increasing current is due to a large contribution from the continuum. The duration of the strong continuum closely follows the duration of the current flow. Based on observations of the appearance of the continuum, the time most favorable for spectrochemical use is after the continuous background, originating at the beginning of the discharge, diminishes to some low value.

2) Variation of line width with time - The time-resolved spark spectra show that some lines vary greatly in width with the time of the discharge. Superimposed on the continuum are some lines which are highly broadened and, in many cases, unresolved. The broadening is due to the Stark effect, resulting from the ion concentration in the gap and to the higher pressure prevailing in the gap at the beginning of the spark discharge. Not visually evident from the spectra in the previous figure are wavelength shifts which accompany the broadening of some lines. Experimental arrangements very similar to that used in this investigation have been used to study the wavelength shift of spectrum lines in spark spectra.[7] The shift always is greatest at the beginning of the spark dis-

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7. Bardocz, A., Vanyek, U. M. and Voros, T., J. Opt. Soc. Amer. 51, 283 (1961).

charge. The observation and evaluation of these effects make possible a more judicious selection of lines for spectrochemical analysis.

3) Order of appearance of spectral lines - The earliest investigations[8] on the order of appearance of different spectrum lines, continuous radiation, and band spectra showed that air lines appear before spark lines and spark lines before arc lines. In spectrochemical analysis, it is most often desirable to use arc lines as analytical lines. If such lines are available for use, then the elimination of early light would greatly reduce any interference from air lines or spark lines. The fact remains that some spark lines show very long radiation lifetimes which permit their use as analysis lines with some improvement in line-to-background ratio over total light exposures because of the elimination of the continuous background radiation. One has to remain cognizant of the fact that the line intensity is continually diminishing in time and the most useful late light is generally of low intensity.

Quantitative Observations. Several factors which can affect the line-to-background ratio must be considered to evaluate quantitatively any improvement in sensitivity. The factors are appropriately categorized under volatilization of sample and excitation of sample. Both are greatly dependent on the source being used and the excitation efficiency depends on the volatilization behavior. Of greatest interest in the application of time-resolved spectroscopy is the excitation behavior. It is desirable that the wanted signals be as high as possible while the unwanted signals are minimized. The random variations in the excitation should be small. The

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8. Schuster, A. and Hemsalech, G., op. cit.

utilization of time-resolved spectra depends on the fact that the decay rate of the unwanted radiation (background) is different from that of the wanted radiation. Figure 11 shows pictorially a situation where time resolution offers some advantages. The background continuum and gaseous line and band spectra decay to relatively low values at a faster rate than the desired line intensity.

Many experiments were made to maximize the wanted signals for several elements of interest using the coated graphite electrodes. These included parameters such as voltage, inductance, gaseous atmospheres (composition and flow rate), gap spacing, and several other miscellaneous parameters. The ones of greatest interest are discussed here. For a given set of excitation parameters, the largest differences in volatilization and excitation behavior were found with changes in the gaseous atmosphere. The pertinent source and excitation parameters are shown in Table I. Figure 12 shows the variations in the intensity of the aluminum arc line AlI 3961.5 for four atmospheres. The behavior of a spark line is shown in Figure 13 with LaII 3949.1. Another arc line GaI 4033.0 is shown in Figure 14 as typical of the behavior of the matrix material. The following features are noted:

a. The peak intensity is reached 5 to 10 $\mu$sec. after the peak of the current flow for the particular region of the gap where the observations were made.

b. The shapes of the curves are similar for the arc lines.

c. The decay rate for the spark line is more rapid than the decay rate for the arc lines.

d. The decay rate in oxygen is more rapid than for the other atmospheres.

TABLE I

EXPERIMENTAL PARAMETERS FOR ROTATING MIRROR EXPOSURES

| | |
|---|---|
| Spectrograph | Baird 3-meter Eagle mounting |
| Slit width | 25 $\mu$ |
| Capacitance | 0.04 $\mu$F |
| Inductance | 180 $\mu$H |
| Voltage | 10 kv |
| Discharge/Cycle | 1 |
| Current flow | 9 $\mu$sec. |
| Counter electrode | 1/4-inch graphite, flat end |
| Sample electrode | 1/4-inch graphite containing 2.5 $\mu$g. each element |
| Analytical gap | 3 mm., light sampled from zone near cathode |
| Atmosphere composition | Air, Argon, Helium, or Oxygen |
| Flow rate | 4 liters/minute |
| Pressure | 580 torr |
| Exposure time | 10 minutes |
| Emulsion | 103-0 |

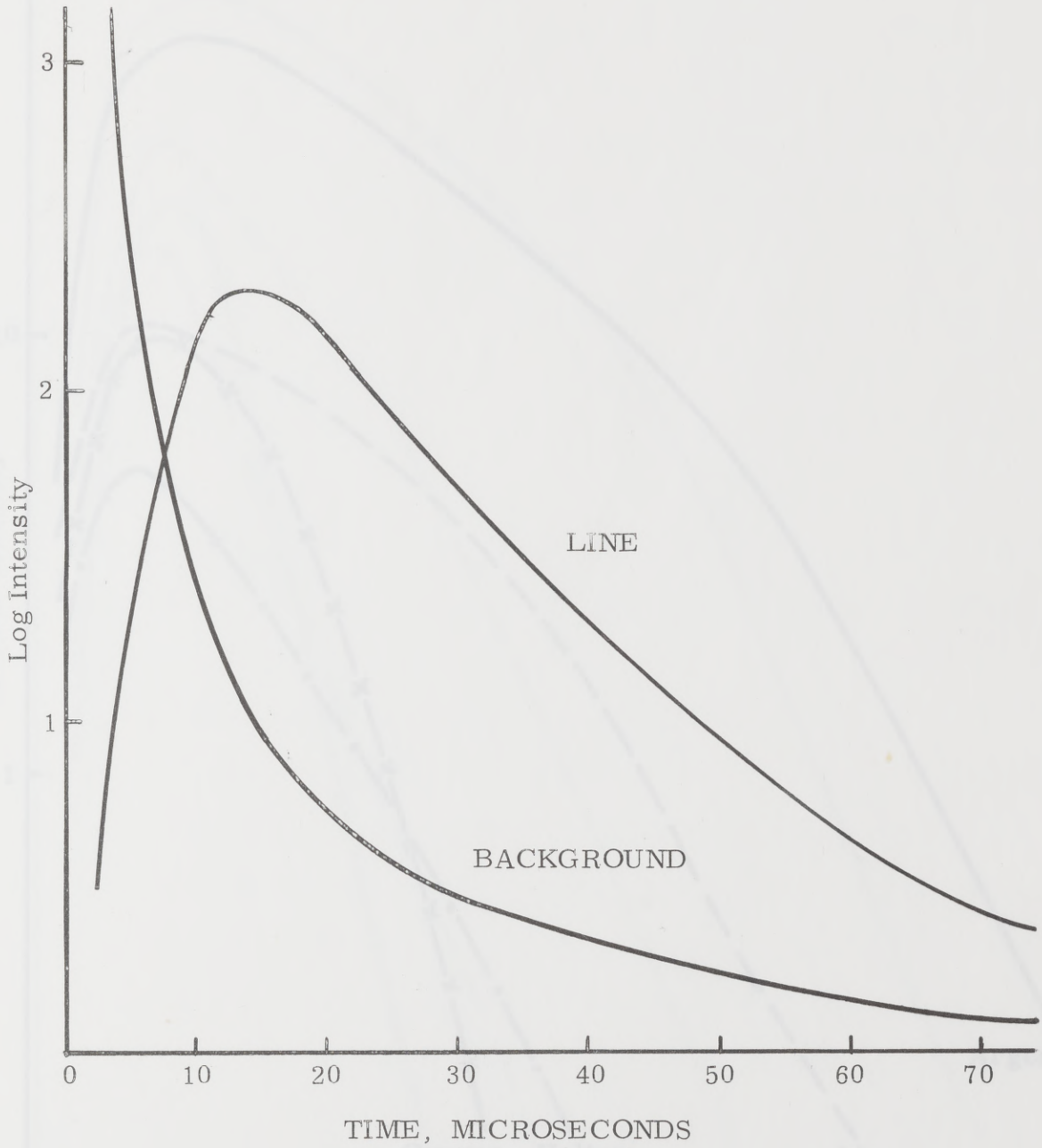


Figure 11. Typical time history of spectral line and background.

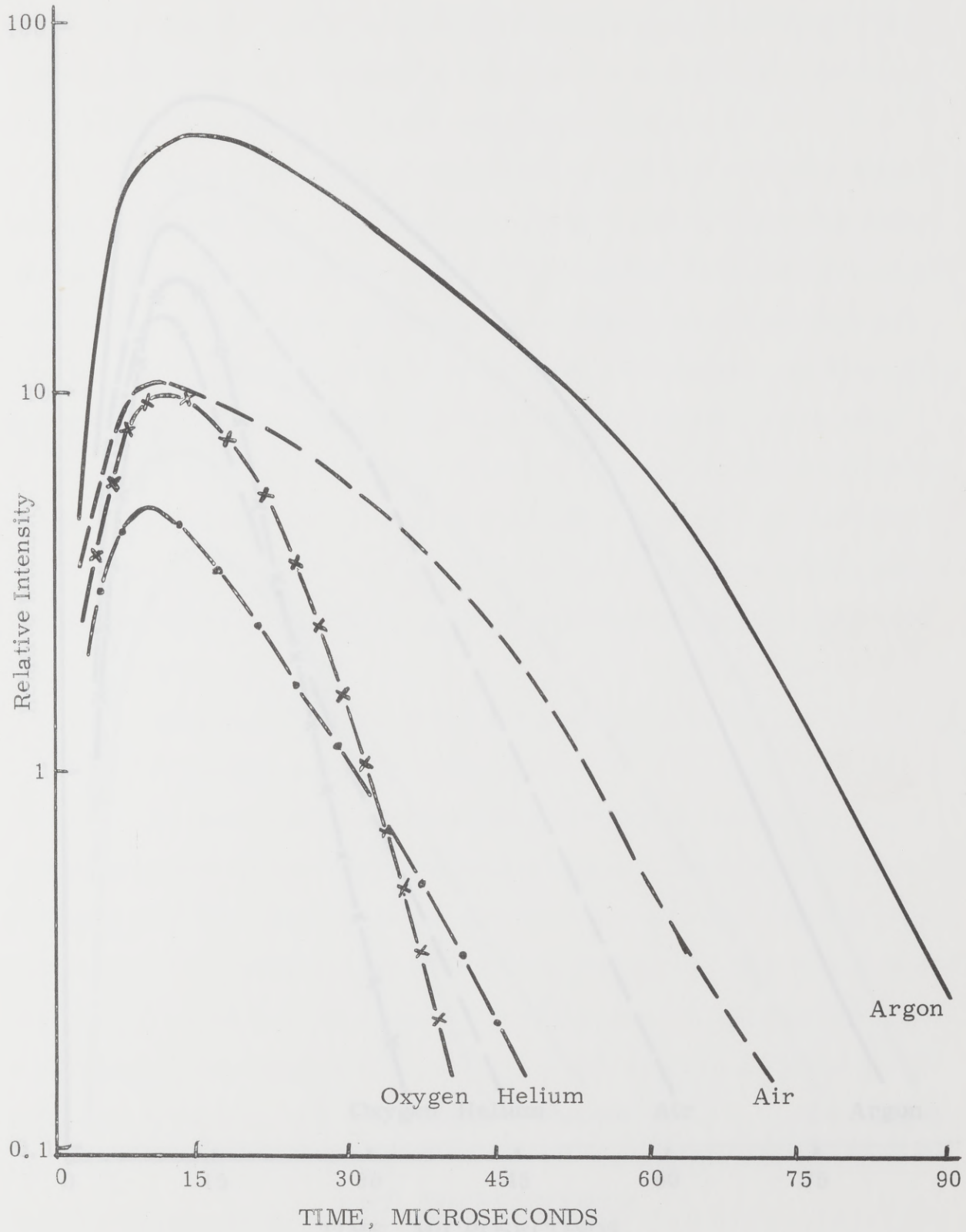


Figure 12. Intensity variations of aluminum arc line for four different atmospheres; Al I 3961.5 (112-25348 K).

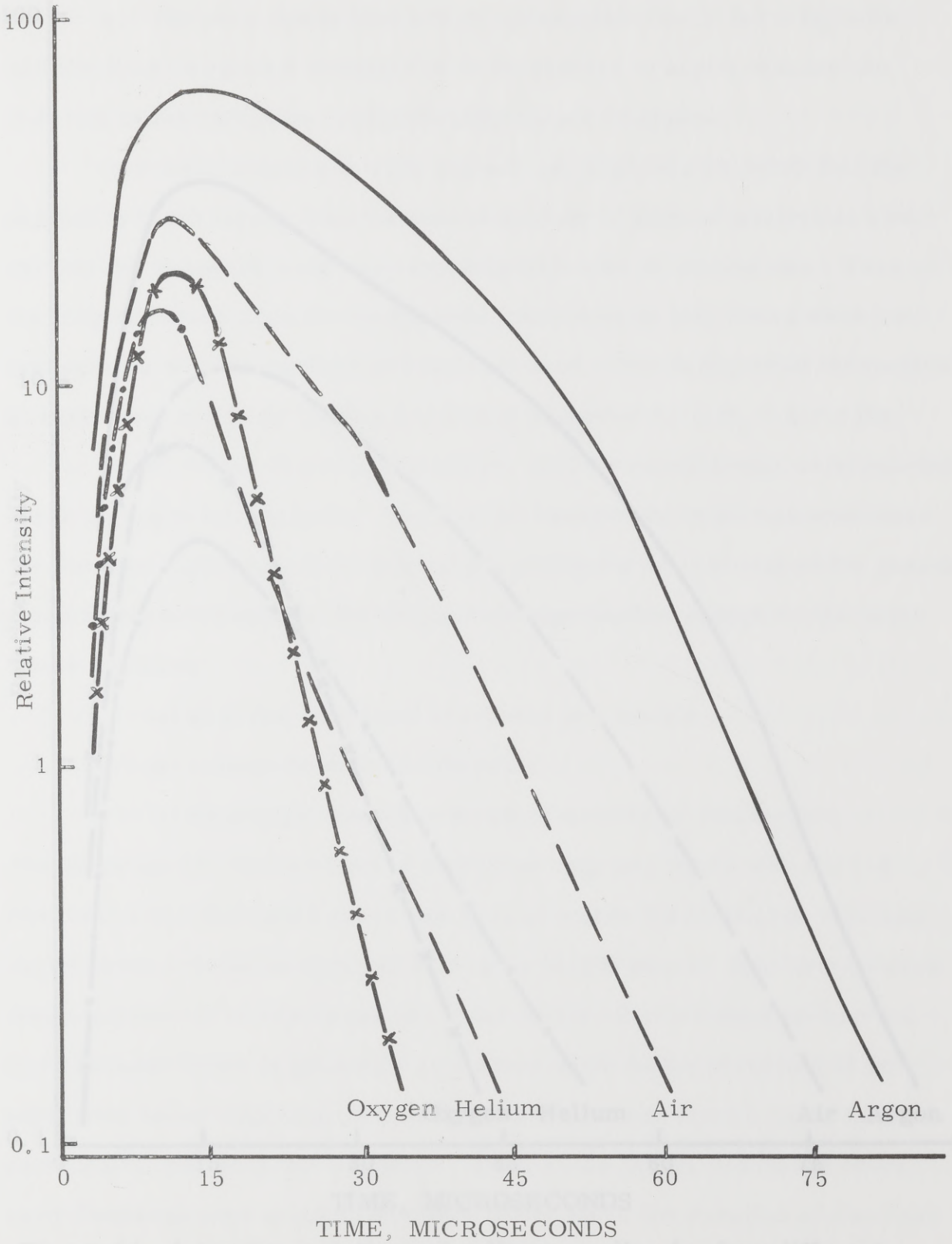


Figure 13. Intensity variations of lanthanum spark line for four different atmospheres; LaII (3250-28565 K).

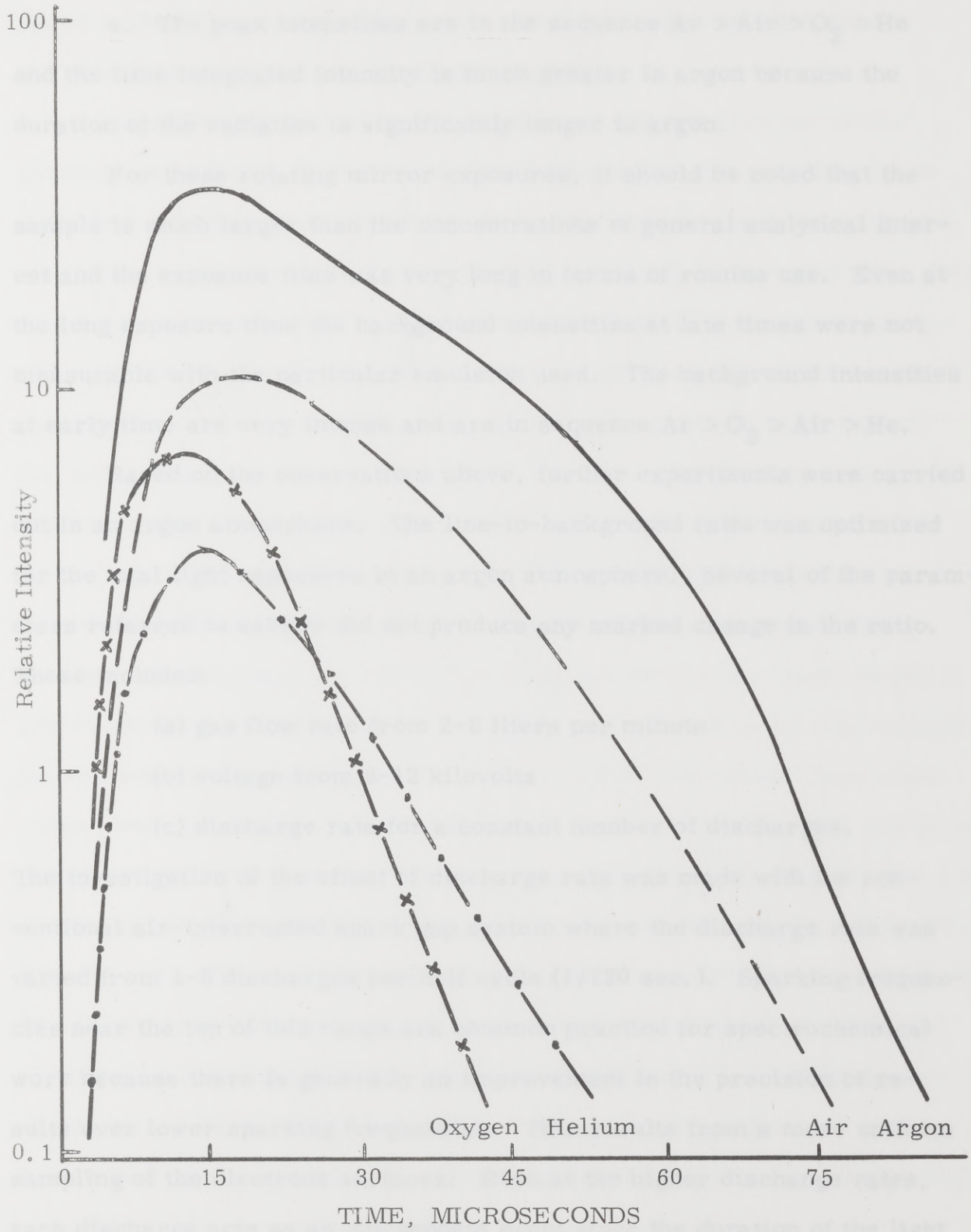


Figure 14. Intensity variations of gallium arc line for four different atmospheres; Gal 4033.0 (0-24788 K).

e. The peak intensities are in the sequence Ar > Air > $O_2$ > He and the time integrated intensity is much greater in argon because the duration of the radiation is significantly longer in argon.

For these rotating mirror exposures, it should be noted that the sample is much larger than the concentrations of general analytical interest and the exposure time was very long in terms of routine use. Even at the long exposure time the background intensities at late times were not measurable with the particular emulsion used. The background intensities at early time are very intense and are in sequence Ar > $O_2$ > Air > He.

Based on the observations above, further experiments were carried out in an argon atmosphere. The line-to-background ratio was optimized for the total light exposures in an argon atmosphere. Several of the parameters referred to earlier did not produce any marked change in the ratio. These included:

(a) gas flow rate from 2-8 liters per minute

(b) voltage from 8-12 kilovolts

(c) discharge rate for a constant number of discharges.

The investigation of the effect of discharge rate was made with the conventional air-interrupted spark gap system where the discharge rate was varied from 1-8 discharges per half cycle (1/120 sec.). Sparking frequencies near the top of this range are common practice for spectrochemical work because there is generally an improvement in the precision of results over lower sparking frequencies. This results from a more uniform sampling of the electrode surfaces. Even at the higher discharge rates, each discharge acts as an independent event since the duration of the light phenomena from each discharge of about 100 microseconds is short com-

pared to the time between discharges. For the time resolution studies, the discharge rate was usually 60 per second.

In addition to the excitation differences noted for the particular gaseous atmospheres on the microsecond time scale, the sampling (volatilization) behavior on another time scale must be considered when coated electrodes are used. This time scale involves the total exposure time which may be up to several minutes, or more fundamentally is a certain number of discharges for the particular set of source conditions being used. Typical behavior is shown in Figure 15. As the exposure time is increased, the background rises at a fairly uniform rate while the line intensity rises asymptotically to a constant level. Since the sample is distributed over the surface of the electrode, the efficiency with which the sample is removed determines the line intensity. Because the background is due to the atmospheric gas and the electrode material which are present essentially in constant proportions for each discharge, it is expected that the background intensity would be almost a linear function with time. Short exposures where the background intensity is below the threshold of the emulsion cannot be evaluated in terms of a line-to-background ratio although it is not uncommon in spectrochemical work to adjust exposure conditions such that there is not a significant background and eliminate consideration of the background in any calculations. Because of this definite limitation of the time of "effective sampling" for the coated graphite electrodes, additional complications are added to those resulting from the fact that the most useful light is diminished in intensity. Exposure times using time resolution must be of this duration or slightly longer.

The porosity of graphite was mentioned as a potential disadvantage

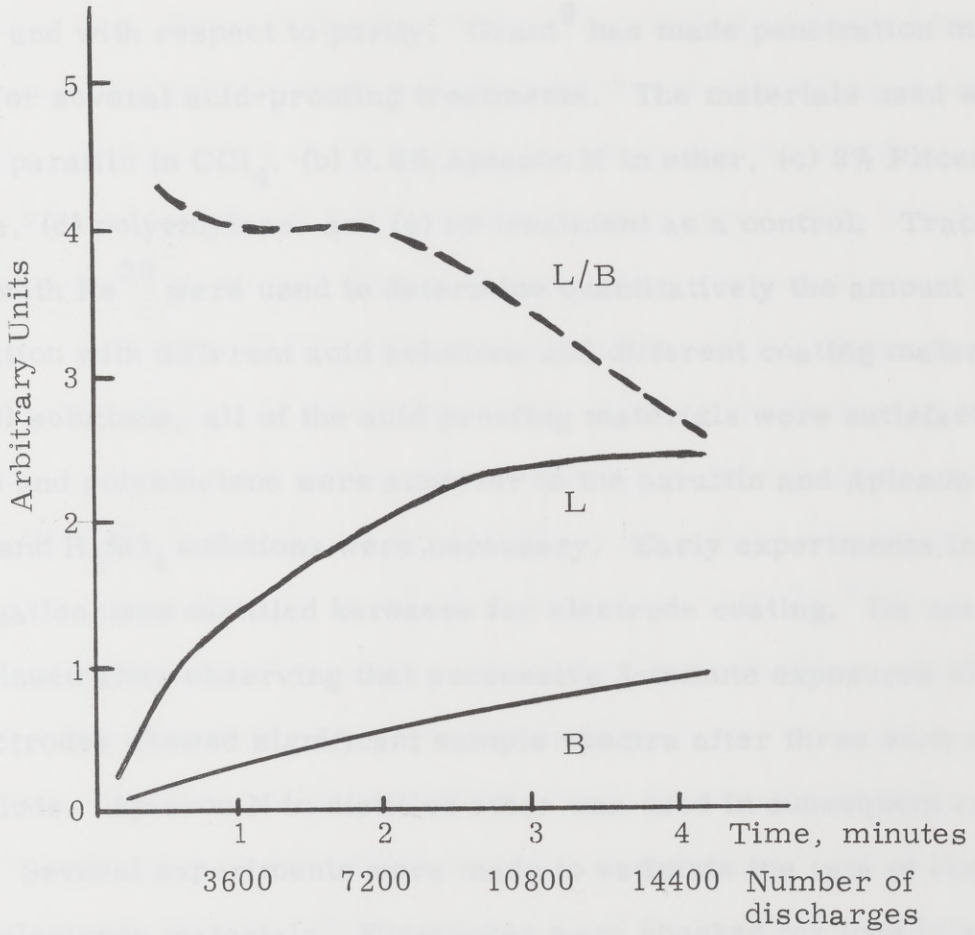


Figure 15. Total light behavior with varying exposure times; coated graphite electrodes, argon atmosphere; light sampled at midplane of 3 mm. gap.

for its use. With the use of graphite, individual investigators usually find some convenient material as a coating to prevent the seepage of solutions downward into the electrode. Many coating materials have been reported in the literature and several coatings are undoubtedly of equal quality as a sealant and with respect to purity. Grant[9] has made penetration measurements for several acid-proofing treatments. The materials used were (a) 10% paraffin in $CCl_4$, (b) 0.5% Apiezon N in ether, (c) 2% Plicene in benzene, (d) polyethylene, and (e) no treatment as a control. Tracer techniques with $Fe^{59}$ were used to determine quantitatively the amount of penetration with different acid solutions and different coating materials. For HCl solutions, all of the acid proofing materials were satisfactory. Plicene and polyethylene were superior to the paraffin and Apiezon N if $HClO_4$ and $H_2SO_4$ solutions were necessary. Early experiments in this investigation used distilled kerosene for electrode coating. Its use was discontinued after observing that successive 3-minute exposures of sample electrodes showed significant sample spectra after three such sparking periods. Apiezon N in distilled ether was used in subsequent experiments. Several experiments were made to estimate the rate of consumption of electrode materials. Electrodes were checked for loss of weight after sparking periods of 30, 60, 90, 120, and 180 seconds. The results show a linear increase in electrode consumption with excitation time for the times 60 to 180 seconds. The short exposure shows a slightly higher rate of consumption probably due to local "high" spots on the electrode surface which are ejected with the first discharges.

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9. Grant, C. L., op. cit.

The use of gallium as a matrix material has already been mentioned. One set of solutions used for this investigation contained the impurities of interest along with gallium at a concentration of 50 $\mu$g./100 $\mu$l. (100 $\mu$l. is the normal size sample). Another set contained only the impurities of interest. The addition of a matrix material is common practice in spectrochemical work because of improvements in volatilization and reproducibility. With the use of the argon atmosphere and the spark discharge, there is also a lowering of the excitation temperature. This is evident by comparing the ratio of MgII 2802.7 to MgI 2852.1 for exposures with and without the gallium additive. The ratios are 2.9 and 5.0 respectively. The additive aids in establishing conditions which are more favorable for the excitation of neutral atom lines. Even with the additive, the discharge is very spark like and for some elements the most sensitive lines are ion lines. For comparison, a copper arc operating at 5000°K[10] gives a ratio of 0.1 for these magnesium lines. Salts of gallium, indium, silver, and lead are commonly used as additives or buffers.

Based on the results reported above, experiments using the rotating disk were made to determine the relative behavior of the line-to-background ratio for total light exposures and time-resolved exposures. Preliminary studies using the rotating disk showed that $t_1$ (on-time) could not exceed 20 $\mu$sec. with graphite electrodes containing concentrations of interest in this investigation for the particular experimental equipment being used. With $t_1$ greater than 20 $\mu$sec. there was insufficient light to cause a measurable background on the plate. This situation could be im-

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10. Meggers, W. F., Corliss, C. H. and Scribner, B. F., National Bureau of Standards Monograph 32-Part 1, 1961.

proved by several methods of amplification with a given spectrograph or by change to a spectrograph more ideally suited to detecting weak signals. Methods of amplification include the use of a more sensitive detector, photomultiplier or faster photographic emulsions. In this procedure, longer exposures do not provide a means of amplification because of the sample limitation. It would be possible to superimpose the light from several individual electrodes with sample. Further experiments to optimize the on-time parameter for coated graphite electrodes resulted in the use of 10 $\mu$sec. as the on-time.

A summary of the conditions used to evaluate the effect on the line-to-background ratio using time-resolution are given in Table II. Exposures are made such that the background for the time-resolved spectra is easily measurable. Other conditions are optimized in terms of the findings reported above for total light and time-resolved exposures. Generally, the line and background densities are within the linear portion of a calibration curve relating the logarithm of exposure to density. Maximum sensitivity will be achieved if the intensity of the line is as large as possible, and the intensity of the background is just above the threshold for the particular photographic plate being used. Based on this type of calculation, sensitivities for several elements are given in Table III. Figure 16 illustrates the procedure used for comparing the relative sensitivities. The lines evaluated in Table III are not necessarily the most sensitive since the wavelength coverage was limited to 2500-3450 A. region. These sensitivities would be fractional parts per million for a procedure such as the ion-exchange spectrographic procedure[11] where the residue deposited on the

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11. Brody, J. K., Faris, V. P. and Buchanan, R. F., op. cit.

TABLE II

EXPERIMENTAL PARAMETERS FOR ROTATING DISK EXPOSURES

| | |
|---|---|
| Spectrograph | Bausch and Lomb Littrow, quartz optics |
| Slit width | 25 $\mu$ |
| Capacitance | 0.075 $\mu$F |
| Inductance | 135 $\mu$H |
| Voltage | 10 kv |
| Discharge/Cycle | 1 |
| Current flow | 10 $\mu$sec. |
| Counter electrode | 1/4-inch graphite, flat end |
| Sample electrode | 1/4-inch graphite coated with Apiezon N in diethyl ether and sample solutions |
| Analytical gap | 3 mm., light sample at mid-plane of gap |
| Atmosphere | Argon |
| Flow rate | 4 liters/minute |
| Pressure | 580 torr |
| Exposure time | Variable 1.5 to 3 minutes |
| Emulsion | 103-0 |
| On-time | 10 $\mu$sec. |

TABLE III

SENSITIVITIES OF SEVERAL ELEMENTS FOR TOTAL LIGHT AND TIME-SECTORED EXPOSURES

| | | Sensitivity, nanograms[a] | |
|---|---|---|---|
| Element | Wavelength, A. | Total Light | Time-sectored[b] |
| Aluminum I | 3082.2 | 200 | 25 |
| Aluminum I | 3092.7 | 75 | 10 |
| Chromium II | 2677.2 | 50 | 7.5 |
| Chromium II | 2835.6 | 25 | 3.5 |
| Chromium II | 2843.3 | 50 | 5 |
| Iron II | 2599.4 | 25 | 2.5 |
| Nickel I | 3414.8 | 125 | 25 |

a Based on L/B = 0.5

b On-time is 10 $\mu$seconds.

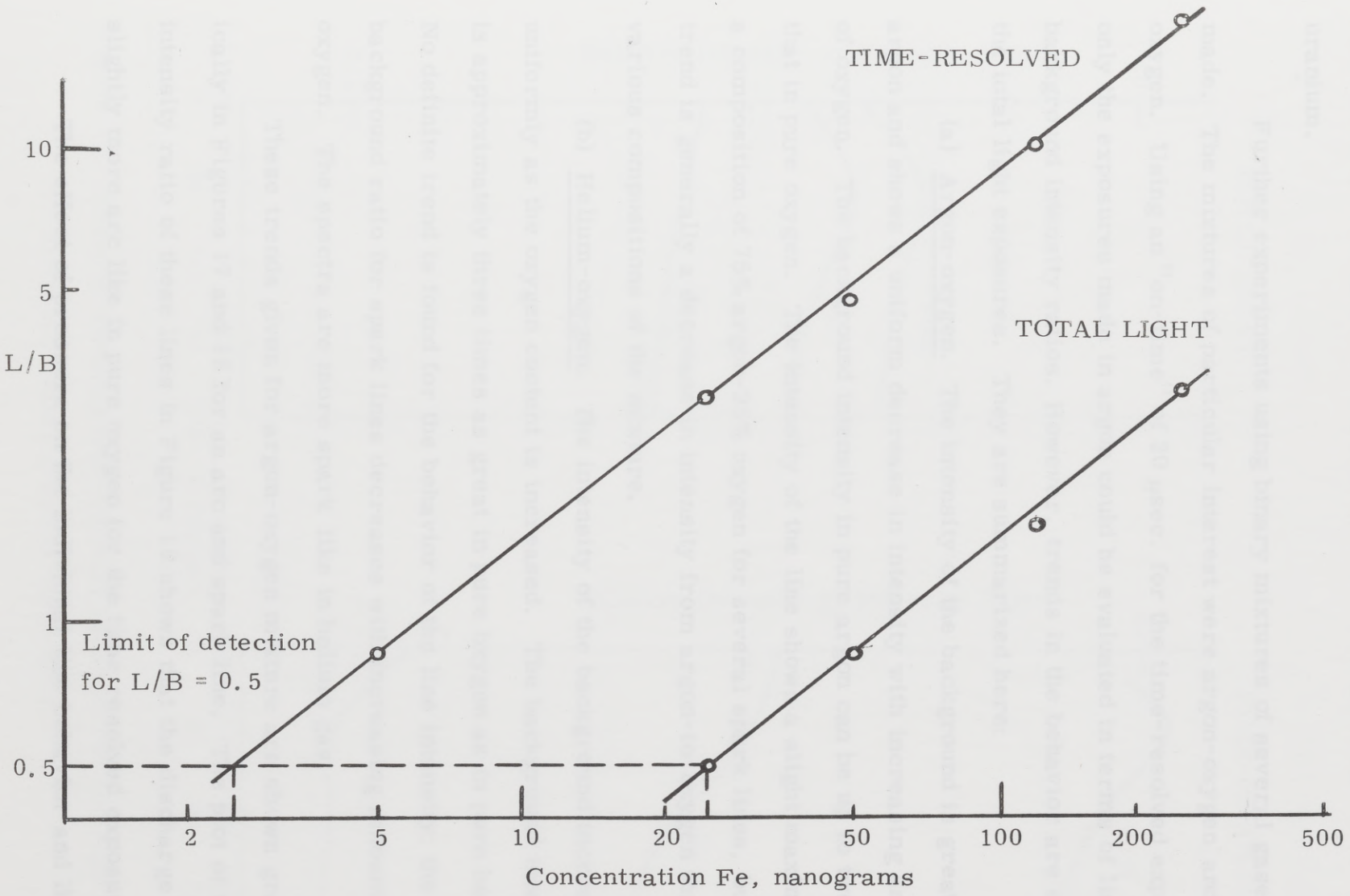


Figure 16. Evaluation of limit of detection for total light and time-resolved exposures FeII 2599.4 (0-38459 K); coated graphite electrodes, argon gas.

electrodes is the impurities separated from 100 mg. of plutonium or uranium.

Further experiments using binary mixtures of several gases were made. The mixtures of particular interest were argon-oxygen and helium-oxygen. Using an "on-time" of 20 $\mu$sec. for the time-resolved exposures, only the exposures made in argon could be evaluated in terms of line-to-background intensity ratios. However, trends in the behavior are seen in the total light exposures. They are summarized here:

(a) Argon-oxygen. The intensity of the background is greatest in argon and shows a uniform decrease in intensity with increasing amounts of oxygen. The background intensity in pure argon can be up to two times that in pure oxygen. The intensity of the line shows a slight maximum with a composition of 75% argon-25% oxygen for several spark lines, but the trend is generally a decrease in intensity from argon-to-oxygen through various compositions of the mixture.

(b) Helium-oxygen. The intensity of the background increases uniformly as the oxygen content is increased. The background intensity is approximately three times as great in pure oxygen as in pure helium. No definite trend is found for the behavior of the line intensity; the line-to-background ratio for spark lines decreases with increasing amounts of oxygen. The spectra are more spark like in helium gas.

These trends given for argon-oxygen mixture are shown graphically in Figures 17 and 18 for an arc and spark line. The plot of the intensity ratio of these lines in Figure 19 shows that the discharge is slightly more arc like in pure oxygen for the time resolved exposures.

The effect of pressure on the individual line behavior and line-to-

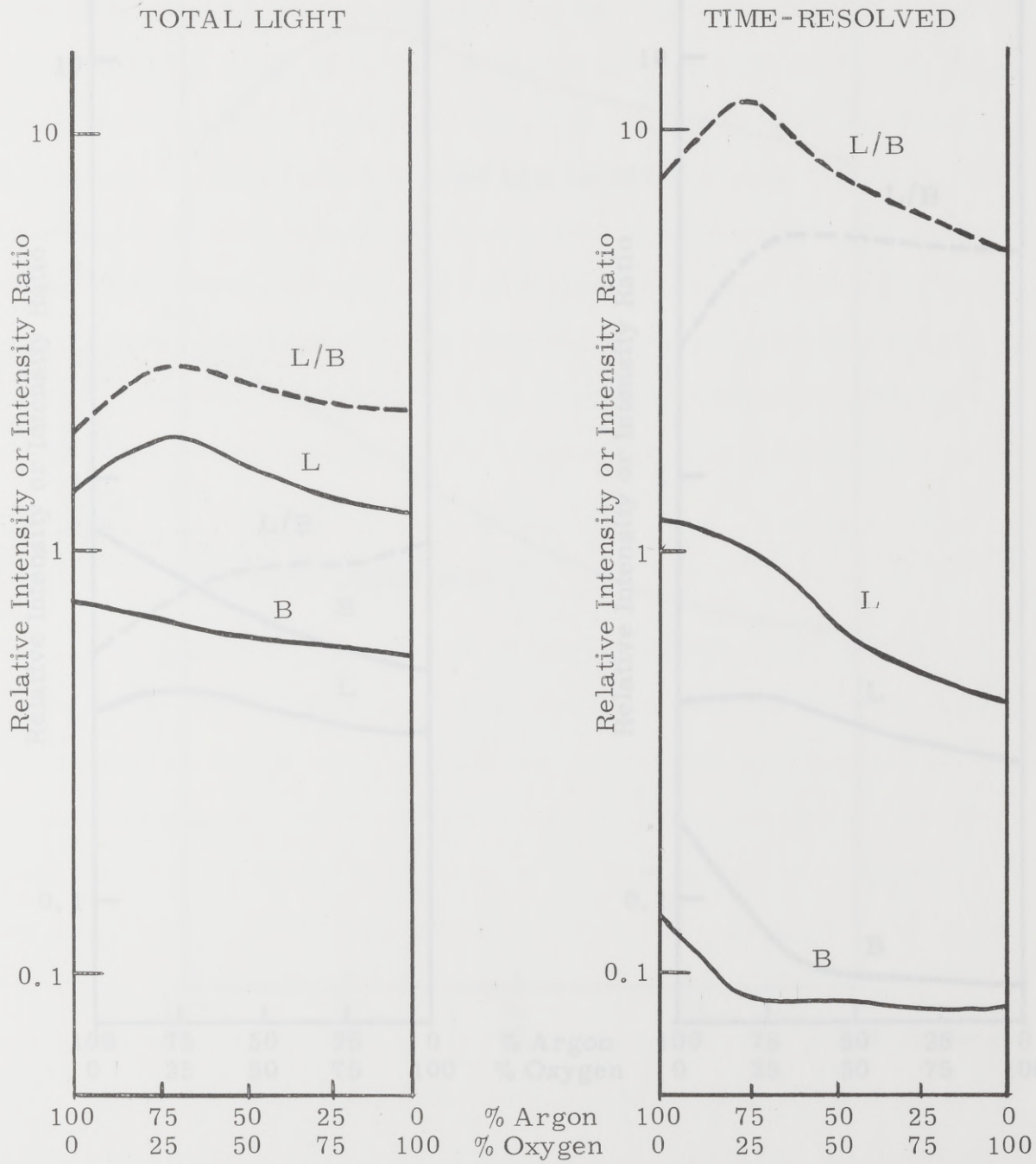


Figure 17. Relative intensity and intensity-ratio curves for MgII 2802.7 (0-35669 K); coated graphite electrodes.

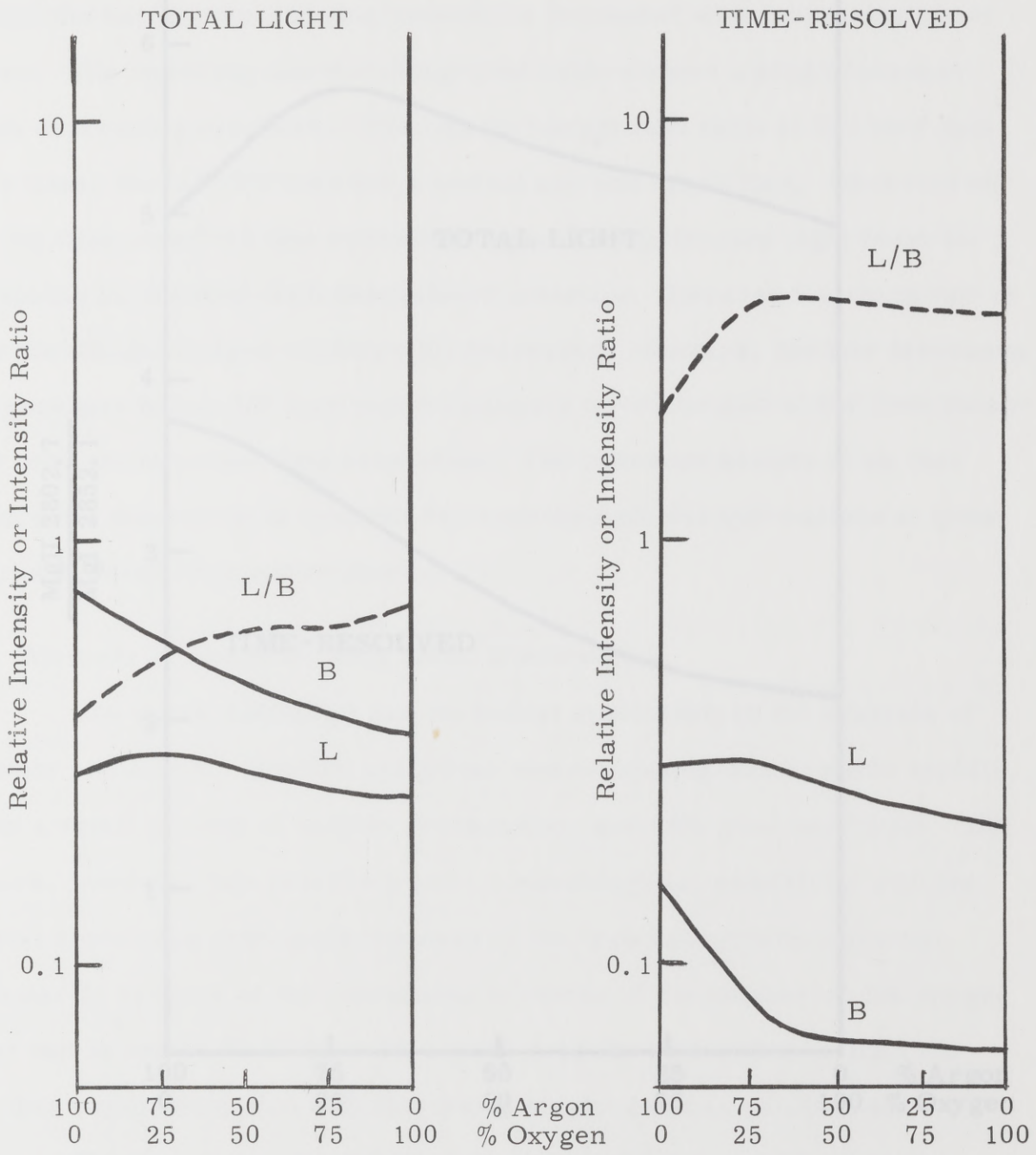


Figure 18. Relative intensity and intensity-ratio curves for MgI 2852.1 (0-35051 K); coated graphite electrodes.

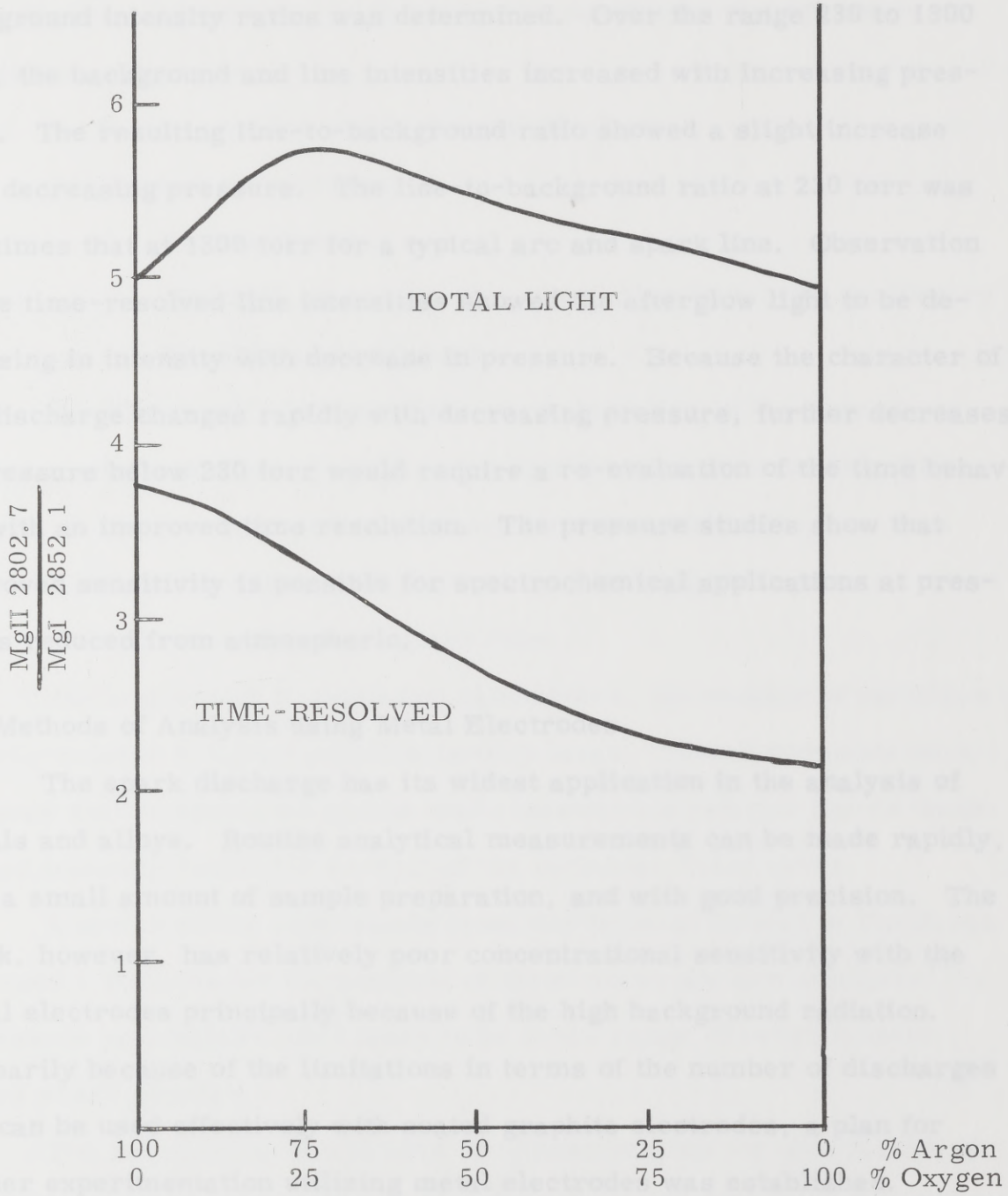


Figure 19. Spark-to-arc ratio curves for total light and time-resolved exposures; coated graphite electrodes containing 5 nanograms Mg.

background intensity ratios was determined. Over the range 230 to 1300 torr, the background and line intensities increased with increasing pressure. The resulting line-to-background ratio showed a slight increase with decreasing pressure. The line-to-background ratio at 230 torr was 1.5 times that at 1300 torr for a typical arc and spark line. Observation of the time-resolved line intensities showed the afterglow light to be decreasing in intensity with decrease in pressure. Because the character of the discharge changes rapidly with decreasing pressure, further decreases in pressure below 230 torr would require a re-evaluation of the time behavior with an improved time resolution. The pressure studies show that improved sensitivity is possible for spectrochemical applications at pressures reduced from atmospheric.

C. Methods of Analysis using Metal Electrodes

The spark discharge has its widest application in the analysis of metals and alloys. Routine analytical measurements can be made rapidly, with a small amount of sample preparation, and with good precision. The spark, however, has relatively poor concentrational sensitivity with the metal electrodes principally because of the high background radiation. Primarily because of the limitations in terms of the number of discharges that can be used effectively with coated graphite electrodes, a plan for further experimentation utilizing metal electrodes was established.

There are many variables associated with the establishing and testing of a spectrographic method using spark excitation. Correlations among various parameters are often difficult because of differences in the time dependent behavior of the spark resulting from changes in source parameters. For this investigation several variables were selected to be

most important in studying improvement in sensitivity through time-resolution. These are:

(1) Spatial position within the analytical gap

(2) Type of current flow

(a) Unidirectional

(b) "Hybrid", a combination of uni-directional and oscillatory

(c) Traditional oscillatory

(3) "On-time", the time from spark initiation to the time where light is allowed to reach the spectrograph (the rotating disk system was used exclusively for these studies)

(4) Gaseous atmosphere surrounding the analytical gap

(5) Behavior of arc and spark lines

For a given set of excitation parameters, the number of variables directly related to time resolution is very large. The experiments here are such that comparisons can be made between the relative line-to-background intensity ratios for several of the variables listed above.

A series of low alloy steels from the National Bureau of Standards was used. Methods for the analysis of these materials are available[12] and source parameters are chosen to be in the range of recommended values where possible.

The gap spacing was divided into three regions for observation of the spatial effects in the gap. The regions were near the cathode (sample electrode), in the center of the gap, and near the anode (counter-electrode) which was either metal or graphite. At the three positions, the background

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12. "Methods of Emission Spectrochemical Analysis", ASTM Publication, Philadelphia, Penna., 1964, p. 157.

intensity is essentially constant for a 3 mm. gap spacing. The largest variations are noted in line intensities. The time integrated line intensities are more intense at the center of the gap. The corresponding line intensities near the anode (counter-electrode) are weaker and more erratic in their behavior with repeated exposures. The line intensities near the cathode are slightly weaker than at the center of the gap. Measurements of the line-to-background intensity ratio resulted in maximum values at the center of the gap based on observations at the three spatial positions. Sampling of the electrode occurs from both electrodes. Tests made with an aluminum and copper electrode pair showed that the radiation at the center of the gap was principally from the aluminum electrode when it was the cathode and the copper electrode the anode. On reversing the polarity from the above, the radiation at the center of the gap was principally due to the copper with the stronger aluminum lines also present. Subsequent experiments are made at the center of the electrode spacing which is 3 mm. unless otherwise stated.

The on-time behavior for several lines is shown in Figures 20 through 24. For these observations an argon atmosphere was used. Comparison of the behavior with the uni-directional and the hybrid source shows only a slight gain in the line intensity for most on-times. The late light is somewhat higher in intensity as is the background. A comparison of the line-to-background intensity ratios shows only a slight gain with the hybrid source. Oscilloscope observations with the hybrid source using graphite electrodes and an air atmosphere showed that the low frequency low current oscillations contributed a significant amount of late light when observations were made in the cyanogen band region. The contributions of late light

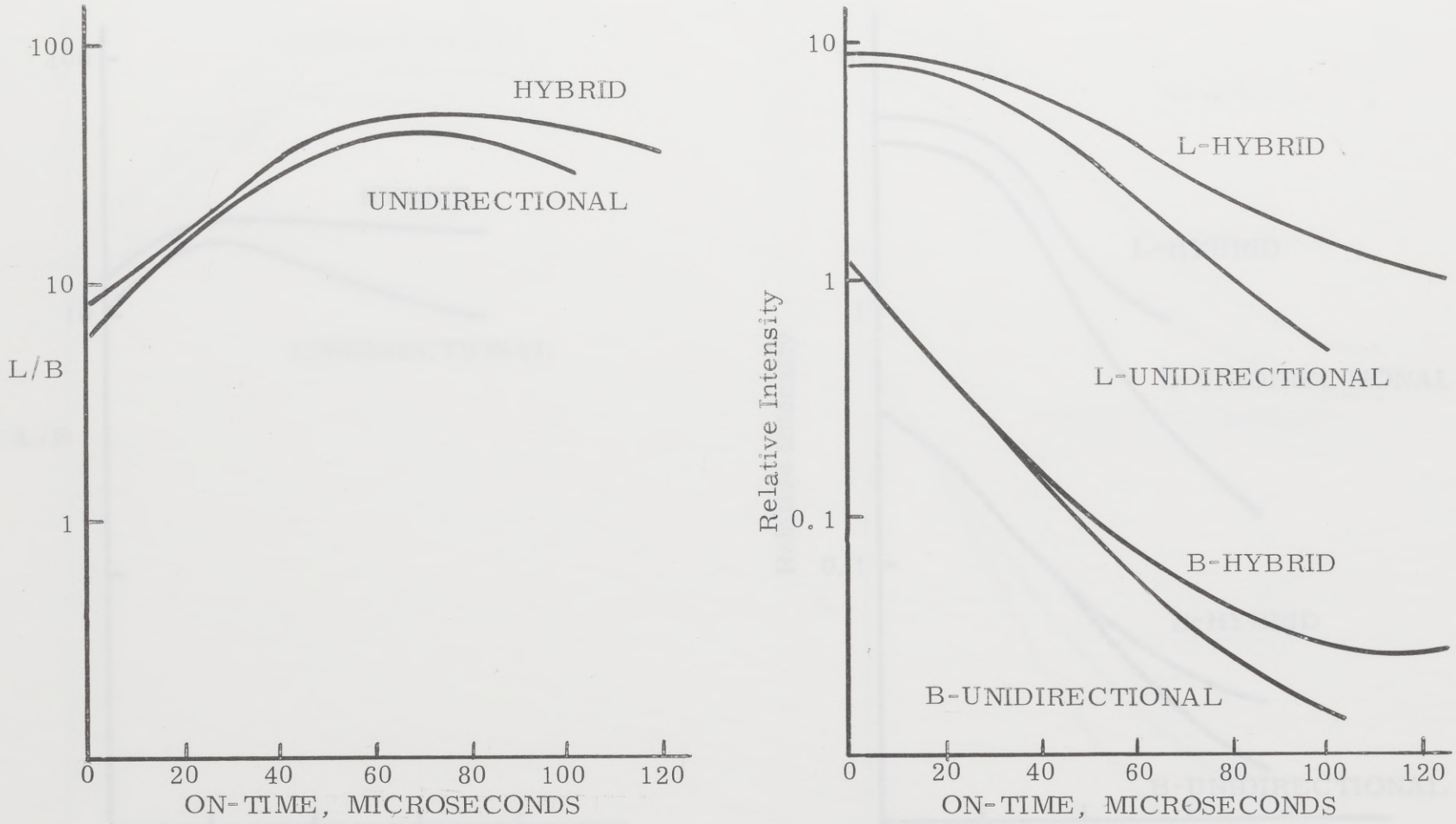


Figure 20. On-time behavior of nickel arc line NiI 3414.8 (205-29481 K); Argon atmosphere, light sampled at midplane of 3 mm. gap.

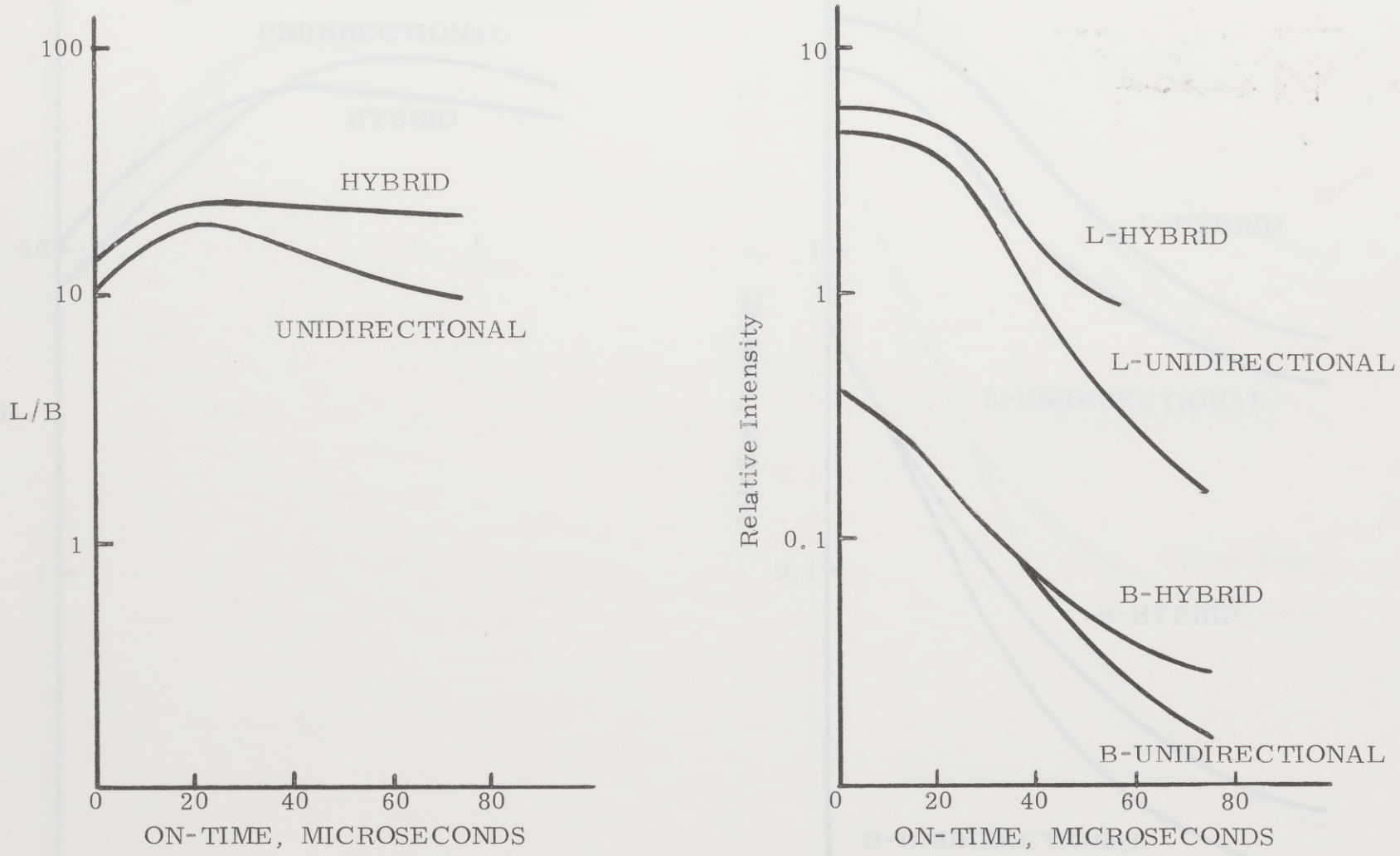


Figure 21. On-time behavior of chromium spark line, CrII 2677.2 (12304-49646 K); Argon atmosphere, light sampled at midplane of 3 mm. gap.

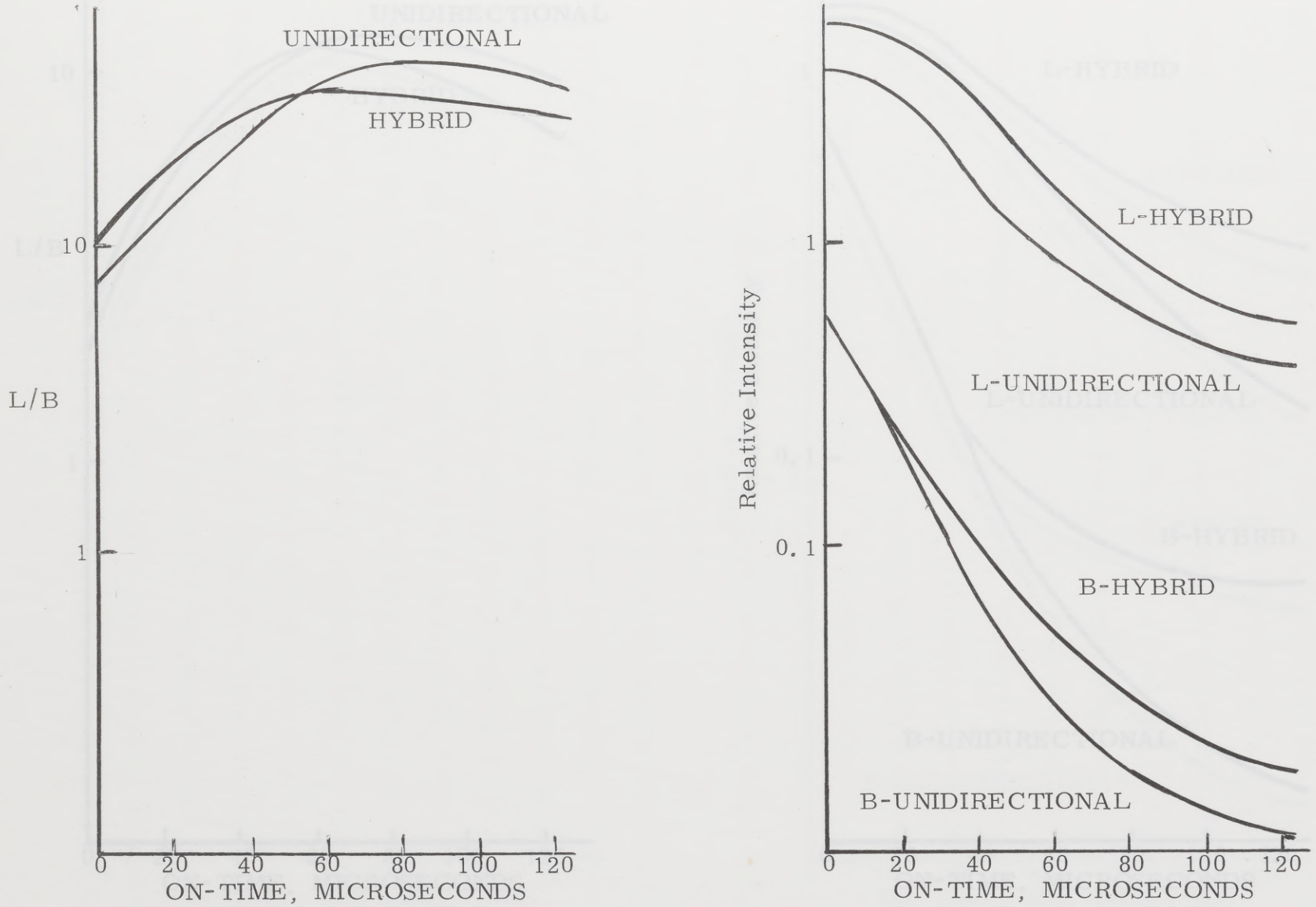


Figure 22. On-time behavior of silicon arc line, SiI 2881.6 (6299-40992 K); Argon atmosphere, light sampled at midplane of 3 mm. gap.

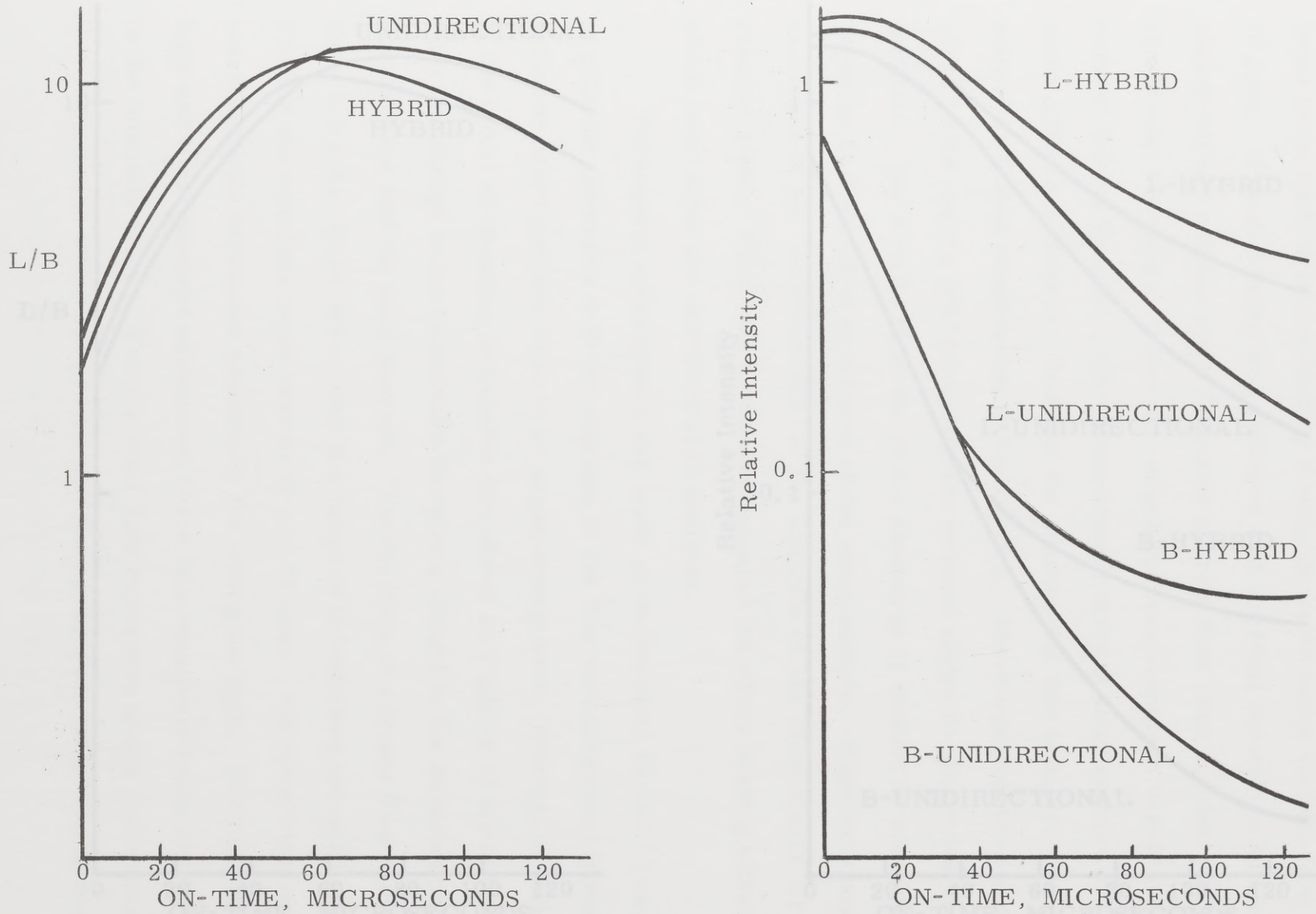


Figure 23. On-time behavior of iron arc line, FeI 2635.8 (7986-45914 K); Argon atmosphere, light sampled at midplane of 3mm. gap.

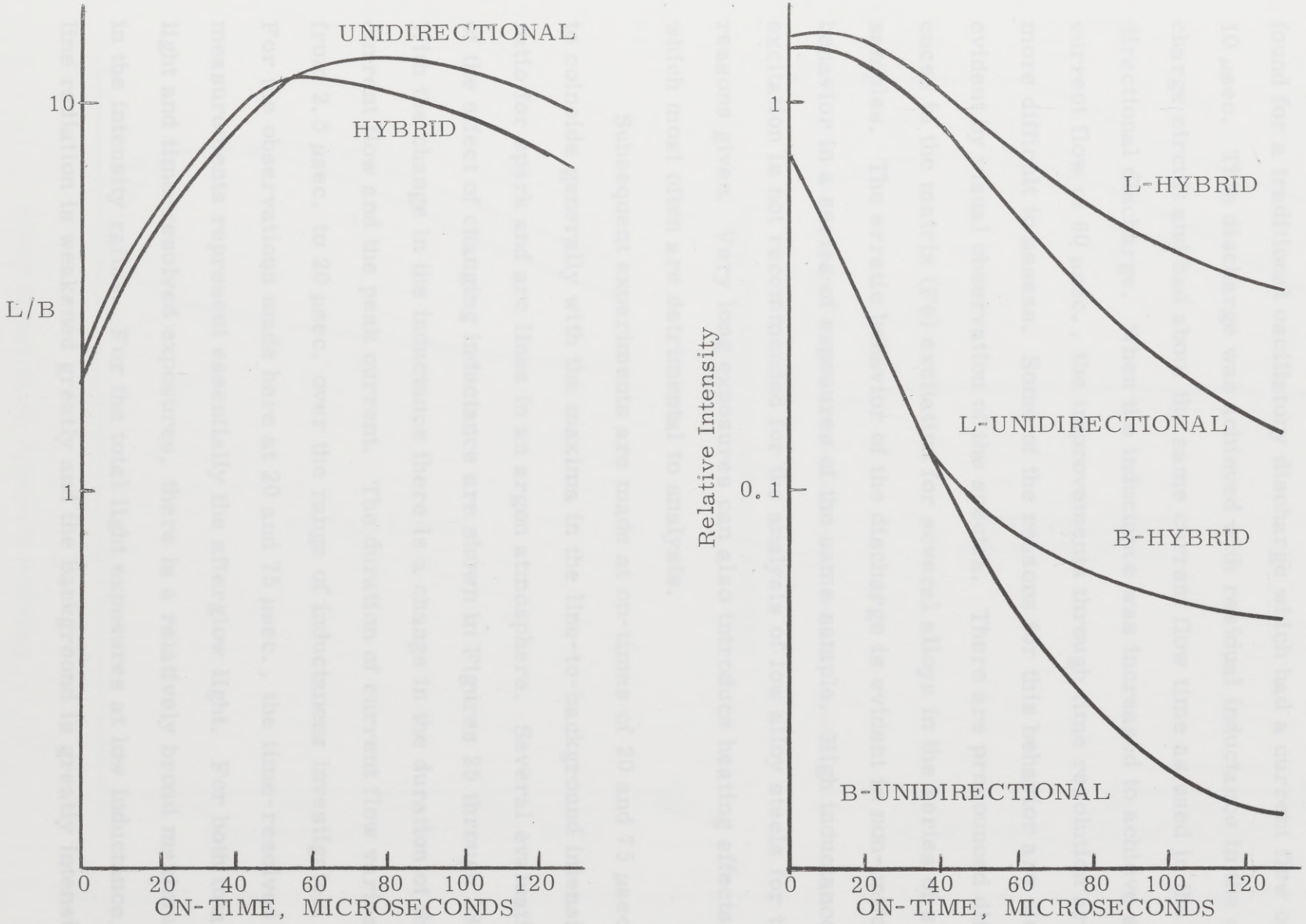


Figure 24. On-time behavior of molybdenum arc line, MoI 3132.6 (0-31943 K); Argon atmosphere, light sampled at midplane of 3mm. gap.

were periodic in behavior in phase with the current. Similar behavior was found for a traditional oscillatory discharge which had a current flow of 10 μsec. This discharge was achieved with residual inductance in the discharge circuit and had about the same current flow time as used in the unidirectional discharge. When the inductance was increased to achieve a current flow of 60 μsec., the improvements through time resolution are more difficult to assess. Some of the reasons for this behavior are clearly evident by visual observation of the spectra. There are pronounced differences in the matrix (Fe) excitation for several alloys in the series of steel samples. The erratic behavior of the discharge is evident in non-uniform behavior in a series of exposures of the same sample. High inductance excitation is not recommended for the analysis of low alloy steels for the reasons given. Very long exposures can also introduce heating effects which most often are detrimental to analysis.

Subsequent experiments are made at on-times of 20 and 75 μsec. to coincide generally with the maxima in the line-to-background intensity ratio for spark and arc lines in an argon atmosphere. Several evaluations of the effect of changing inductance are shown in Figures 25 through 28. With the change in the inductance there is a change in the duration of the current flow and the peak current. The duration of current flow varies from 2.5 μsec. to 20 μsec. over the range of inductances investigated. For the observations made here at 20 and 75 μsec., the time-resolved measurements represent essentially the afterglow light. For both total light and time-resolved exposures, there is a relatively broad maximum in the intensity ratios. For the total light exposures at low inductance, the line radiation is weakened greatly and the background is greatly intensified.

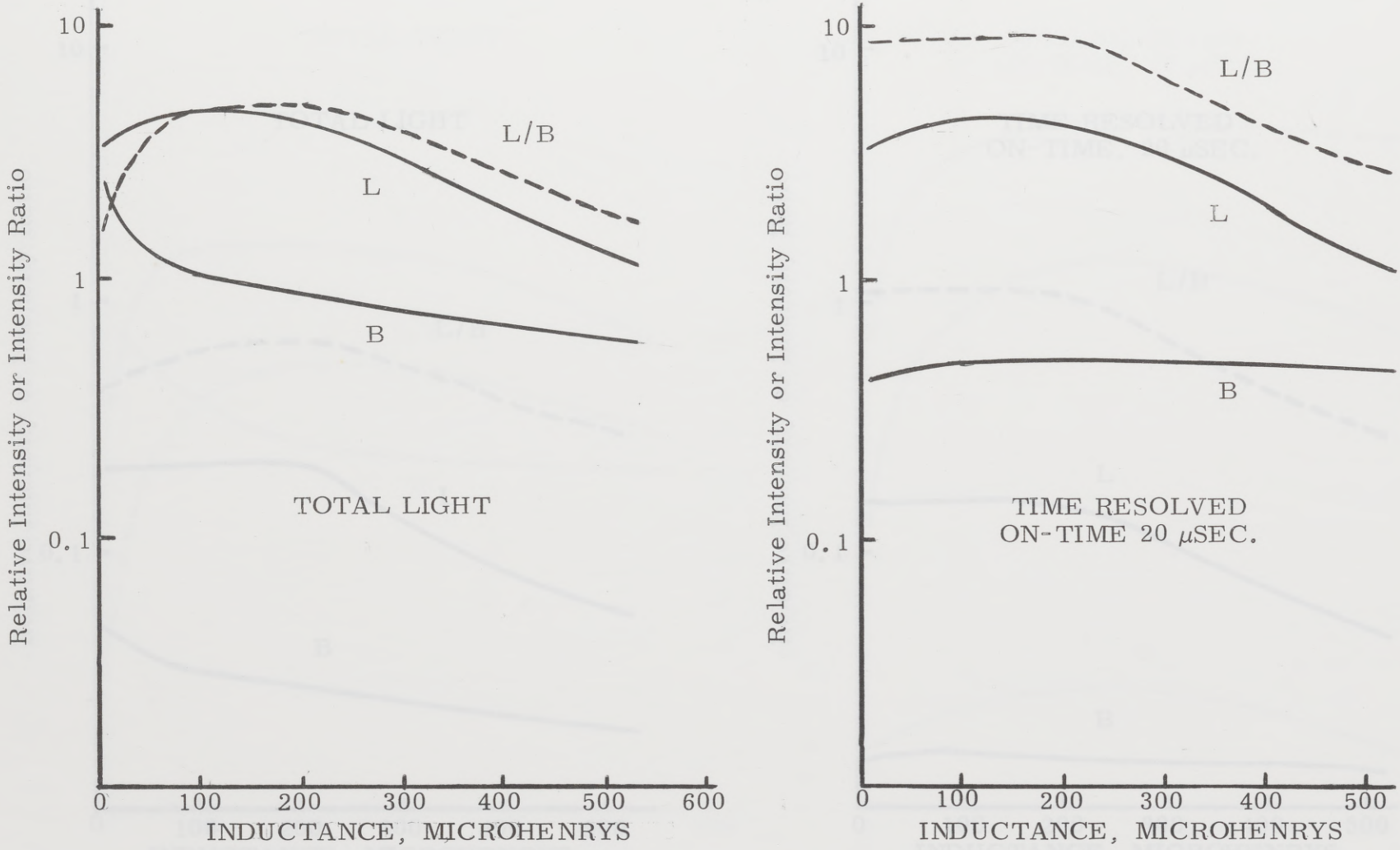


Figure 25. Relative intensity and intensity-ratio curves for NiI 3414.8 with variable inductance; Argon atmosphere, light sampled at midplane of 3 mm. gap; On-time, 20 μsec.

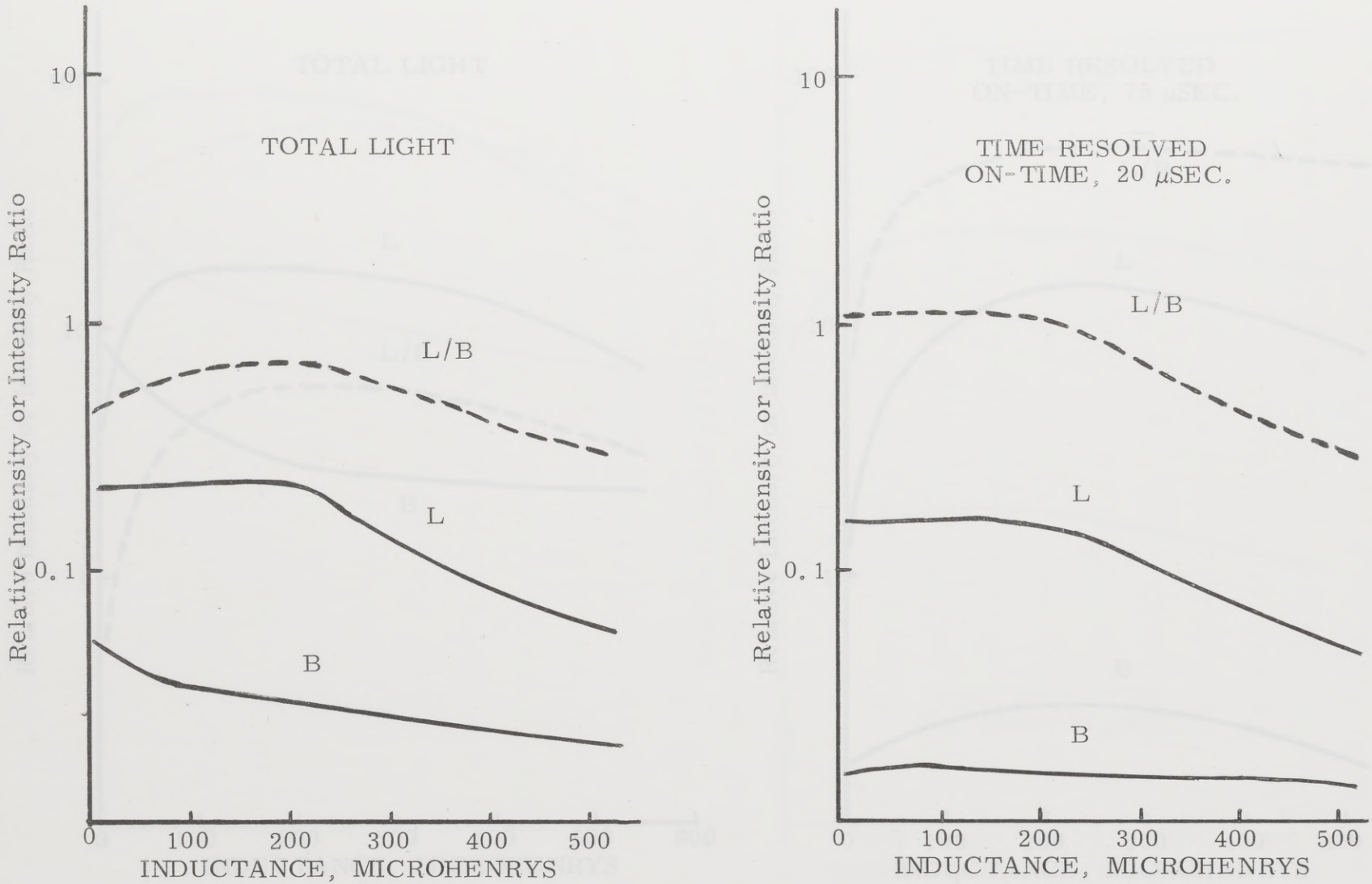


Figure 26. Relative intensity and intensity-ratio curves for CrII 2677.2 with variable inductance; Argon atmosphere, light sampled at midplane of 3 mm. gap; On-time, 20 μsec.

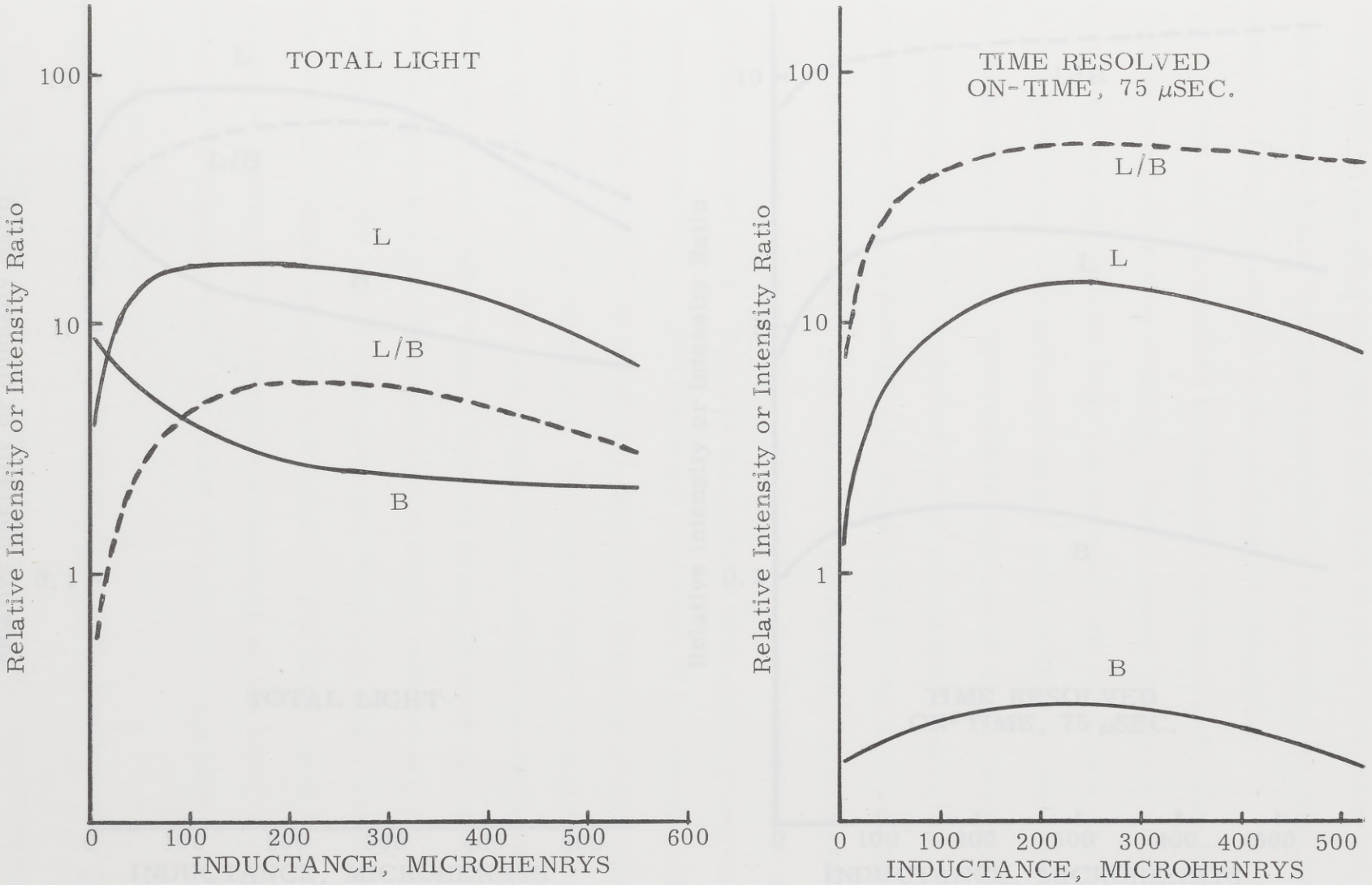


Figure 27. Relative intensity and intensity-ratio curves for NiI 3414.8 with variable inductance; Argon atmosphere, light sampled at midplane of 3 mm. gap; On-time, 75 μsec.

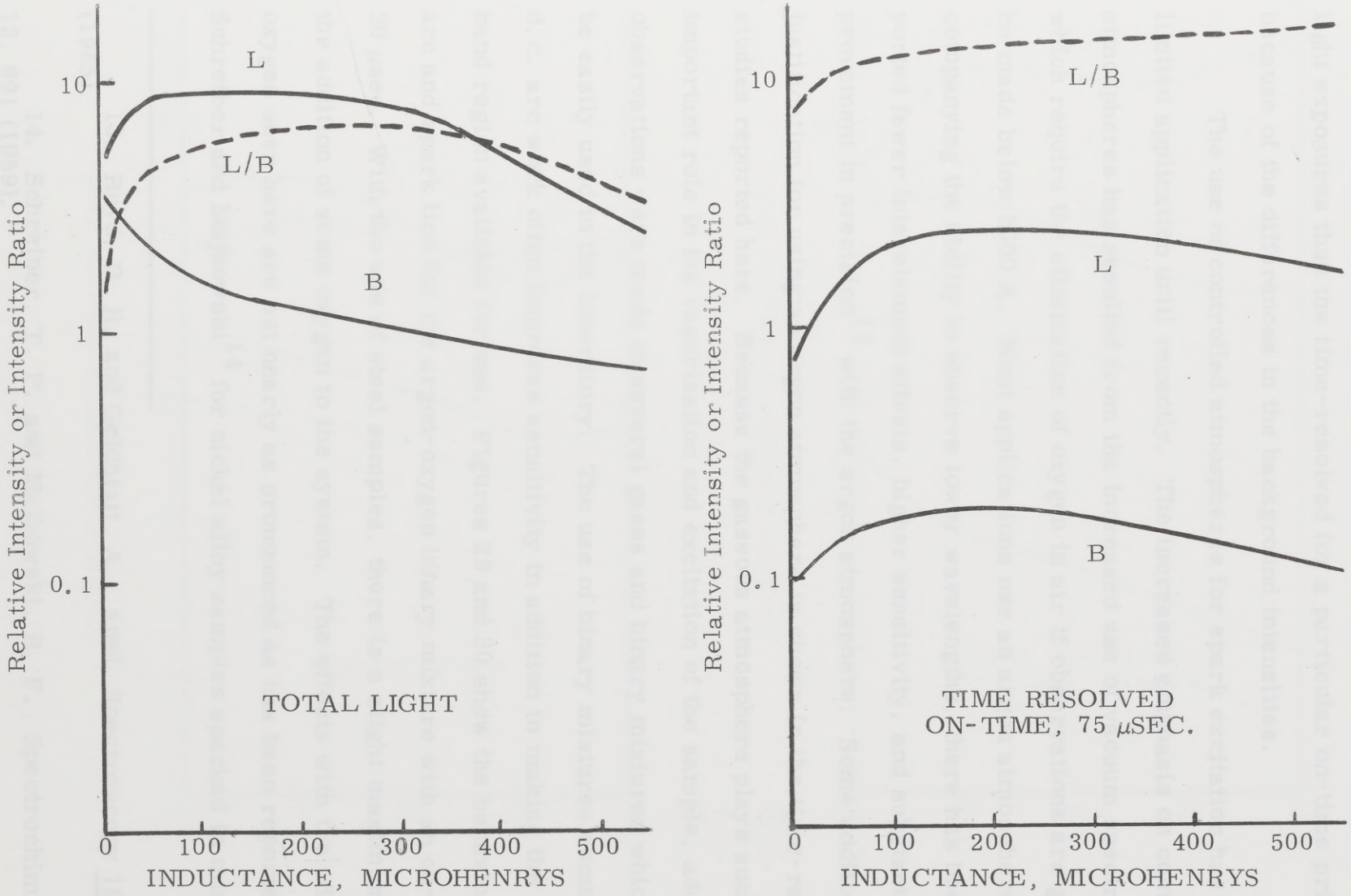


Figure 28. Relative intensity and intensity-ratio curves for CrII 2677.2 with variable inductance; Argon atmosphere, light sampled at midplane of 3 mm. gap; On-time, 75 μsec.

The effect of changing inductance (current) is more pronounced in the total light exposures than the time-resolved for a particular on-time primarily because of the differences in the background intensities.

The use of controlled atmospheres for spark excitation has had limited application until recently. The increased emphasis on controlled atmospheres has resulted from the increased use of vacuum spectrometers which require the elimination of oxygen in air if observations are going to be made below 2000 A. Most applications use an argon atmosphere. Accompanying the ability to observe lower wavelengths, there has been reported fewer interelement effects, higher sensitivity, and substantial improvement in precision[13] with the argon atmosphere. Some additional justification for using an argon atmosphere is shown in the time-resolved studies reported here. Because the gaseous atmosphere plays such an important role in the vaporization and excitation of the sample, additional observations were made in several gases and binary mixtures which could be easily used in the laboratory. The use of binary mixtures common in d. c. arc work often improves sensitivity in addition to making the cyanogen band region available for use. Figures 29 and 30 show the behavior of an arc and spark line for the argon-oxygen binary mixture with an on-time of 20 $\mu$sec. With the use of steel samples, there is a slight maximum with the addition of some oxygen to the system. The effects with the addition of oxygen seen here are not nearly as pronounced as has been reported by Schreiber and Majkowski[14] for nickel alloy samples sparked in mixtures of

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13. Boyd, B. R. and Goldblatt, A., Appl. Spectroscopy 19, 22 (1965).

14. Schreiber, T. P. and Majkowski, R. F., Spectrochim. Acta 12, 991 (1959).

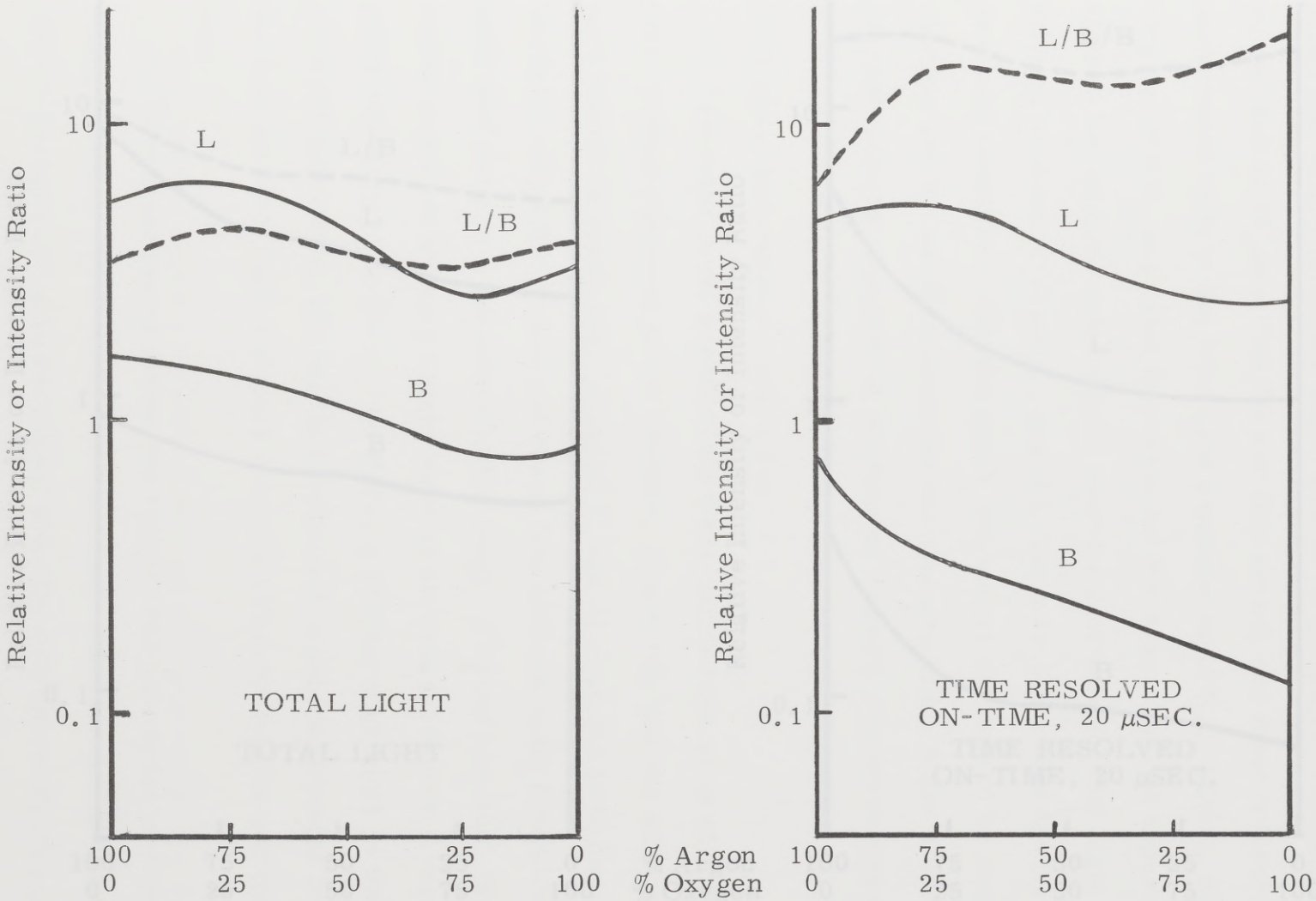


Figure 29. Relative intensity and intensity-ratio curves for NiI 3414.8 for argon-oxygen atmosphere; Light sampled at midplane of 3 mm. gap; On-time, 20 μsec.

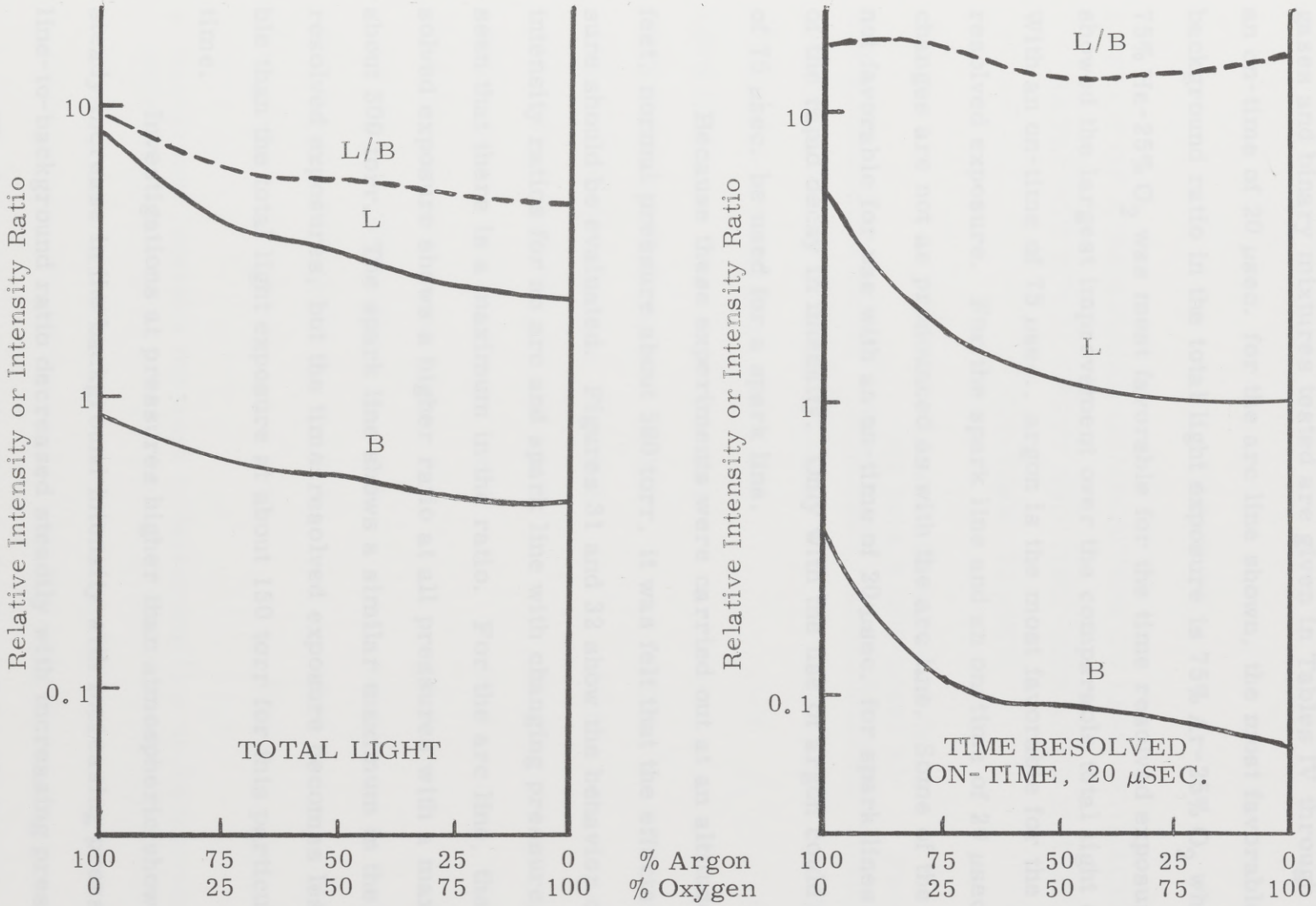


Figure 30. Relative intensity and intensity-ratio curves for CrII 2677.2 for argon-oxygen atmosphere; Light sampled at midplane of 3 mm. gap; On-time, 20 μsec.

oxygen, nitrogen and argon. Summaries of the findings for the several gases and binary mixtures tested are given in Tables IV through VI. With an on-time of 20 μsec. for the arc line shown, the most favorable line-to-background ratio in the total light exposure is 75% Ar-25% $O_2$ while 75% He-25% $O_2$ was most favorable for the time resolved exposures and showed the largest improvement over the comparable total light exposure. With an on-time of 75 μsec., argon is the most favorable for the time-resolved exposure. For the spark line and an on-time of 20 μsec., the changes are not as pronounced as with the arc line. Some of the gases are not favorable for use with an on-time of 20 μsec. for spark lines because of the rapid decay in intensity. Only with the use of argon could an on-time of 75 μsec. be used for a spark line.

Because these experiments were carried out at an altitude of 7,000 feet, normal pressure about 580 torr, it was felt that the effects of pressure should be evaluated. Figures 31 and 32 show the behavior of the intensity ratios for an arc and spark line with changing pressure. It is seen that there is a maximum in the ratio. For the arc line, the time resolved exposure shows a higher ratio at all pressures with a maximum at about 300 torr. The spark line shows a similar maximum in the time-resolved exposures, but the time-resolved exposure becomes less favorable than the total light exposure at about 150 torr for this particular on-time.

Investigations at pressures higher than atmospheric showed a steady increase in the background intensity with increasing pressure. The line-to-background ratio decreased steadily with increasing pressure.

The improvement in the line-to-background ratio by using time

TABLE IV

EFFECT OF ATMOSPHERE COMPOSITION ON LINE-TO-BACKGROUND RATIO FOR TOTAL LIGHT AND TIME-RESOLVED EXPOSURES

ON-TIME, 20 $\mu$SEC.

| Atmosphere Composition[b] | Line-to-Background Ratio NiI 3414.8 (205-29481 K) Total Light | Time-Resolved | Factor of Improvement |
|---|---|---|---|
| 100% Neon | 3.2 | 9.1 | 2.8 |
| 75% Neon-25% Oxygen | 2.6 | 11.5 | 4.4 |
| 100% Helium | 1.4 | a | a |
| 75% Helium-25% Oxygen | 3.6 | 33.4 | 9.3 |
| 50% Helium-50% Oxygen | 3.8 | 24.2 | 6.4 |
| 25% Helium-75% Oxygen | 3.9 | 21.4 | 5.5 |
| 100% Oxygen | 4.5 | 22.2 | 4.9 |
| 75% Oxygen-25% Argon | 3.4 | 12.8 | 3.8 |
| 50% Oxygen-50% Argon | 3.8 | 14.5 | 3.8 |
| 25% Oxygen-75% Argon | 5.3 | 16.1 | 3.0 |
| 100% Argon | 3.7 | 7.5 | 2.0 |

a Background intensity too weak to determine line-to-background ratio reliably.

b Flow system, gas flow rate is 4 liters per minute.

TABLE V

EFFECT OF ATMOSPHERE COMPOSITION ON LINE-TO-BACKGROUND RATIO FOR TOTAL LIGHT AND TIME-RESOLVED EXPOSURES

ON-TIME, 20 $\mu$SEC.

| Atmosphere Composition[b] | Line-to-Background Ratio CrII 2677.2 (12304-49646 K) Total Light | Time-Resolved | Factor of Improvement |
|---|---|---|---|
| 100% Neon | 14.9 | a | |
| 75% Neon-25% Oxygen | 8.0 | a | |
| 100% Helium | 16.2 | a | |
| 75% Helium-25% Oxygen | 9.1 | 18.5 | 2.0 |
| 50% Helium-50% Oxygen | 6.8 | 14.3 | 2.1 |
| 25% Helium-75% Oxygen | 5.6 | 11.7 | 2.1 |
| 100% Oxygen | 5.1 | 12.1 | 2.4 |
| 75% Oxygen-25% Argon | 5.0 | 10.4 | 2.1 |
| 50% Oxygen-50% Argon | 5.8 | 11.5 | 2.0 |
| 25% Oxygen-75% Argon | 6.2 | 14.3 | 2.3 |
| 100% Argon | 4.9 | 10.0 | 2.0 |

a Background intensity too weak to determine line-to-background ratio reliably.

b Flow system, gas flow rate is 4 liters per minute.

TABLE VI

EFFECT OF ATMOSPHERE COMPOSITION ON LINE-TO-BACKGROUND RATIO FOR TOTAL LIGHT AND TIME-RESOLVED EXPOSURES

ON-TIME, 75 μSEC.

| Atmosphere Composition* | Line-to-Background Ratio NiI 3414.8 (205-29481 K) Total Light | Time-Resolved | Factor of Improvement |
|---|---|---|---|
| 75% Helium-25% Oxygen | 3.6 | 27.8 | 7.7 |
| 50% Helium-50% Oxygen | 3.8 | 21.4 | 5.6 |
| 25% Helium-75% Oxygen | 3.9 | 20.8 | 5.3 |
| 100% Oxygen | 4.5 | 21.3 | 4.7 |
| 75% Oxygen-25% Argon | 3.4 | 17.8 | 5.2 |
| 50% Oxygen-50% Argon | 3.8 | 20.7 | 5.4 |
| 25% Oxygen-75% Argon | 5.3 | 20.4 | 3.9 |
| 100% Argon | 3.7 | 44.0 | 12.0 |

* Flow system, gas flow rate is 4 liters per minute.

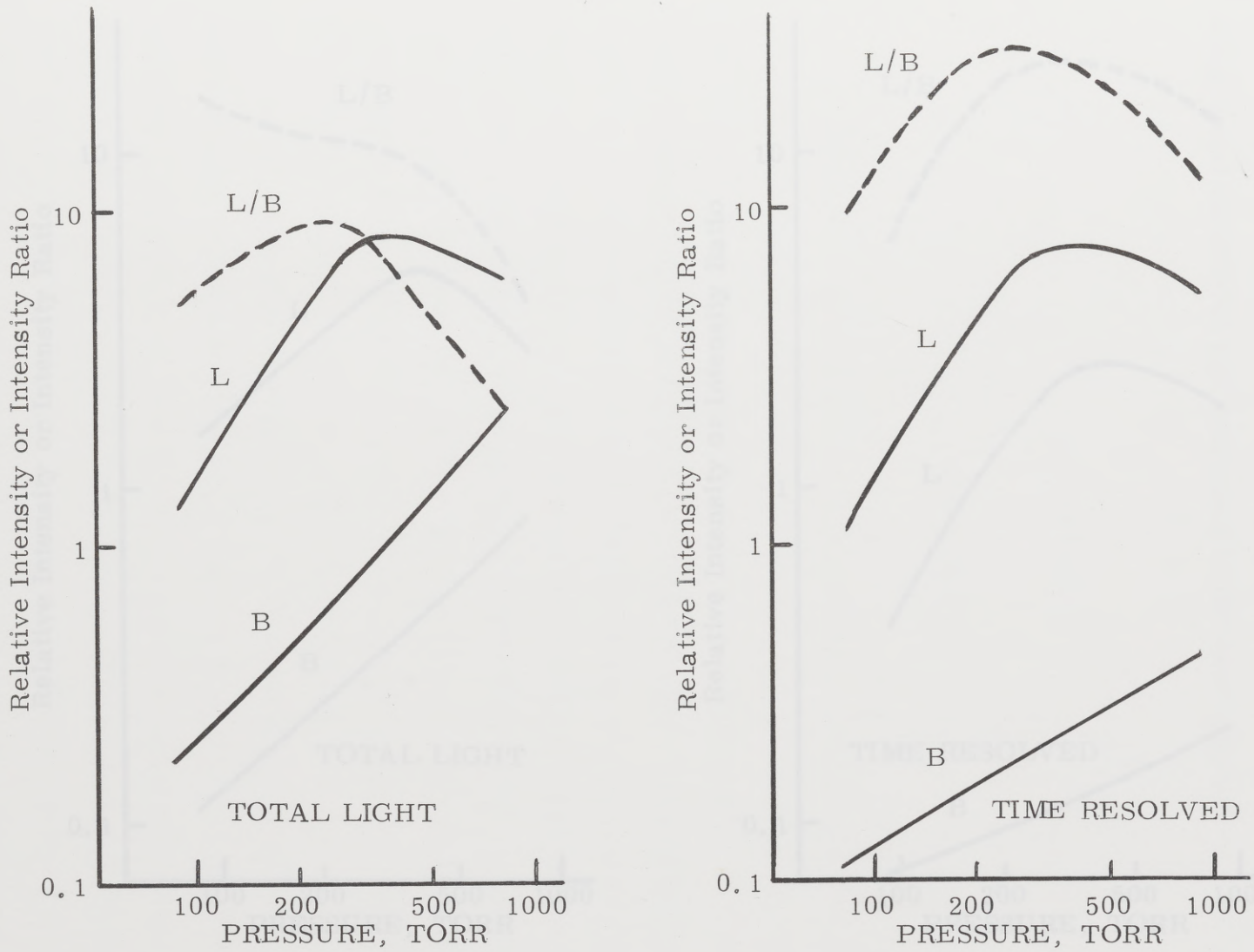


Figure 31. Relative intensity and intensity-ratio curves for NiI 3414.8 with pressure; Light sampled at midplane of 3 mm. gap; On-time, 20 $\mu$sec.

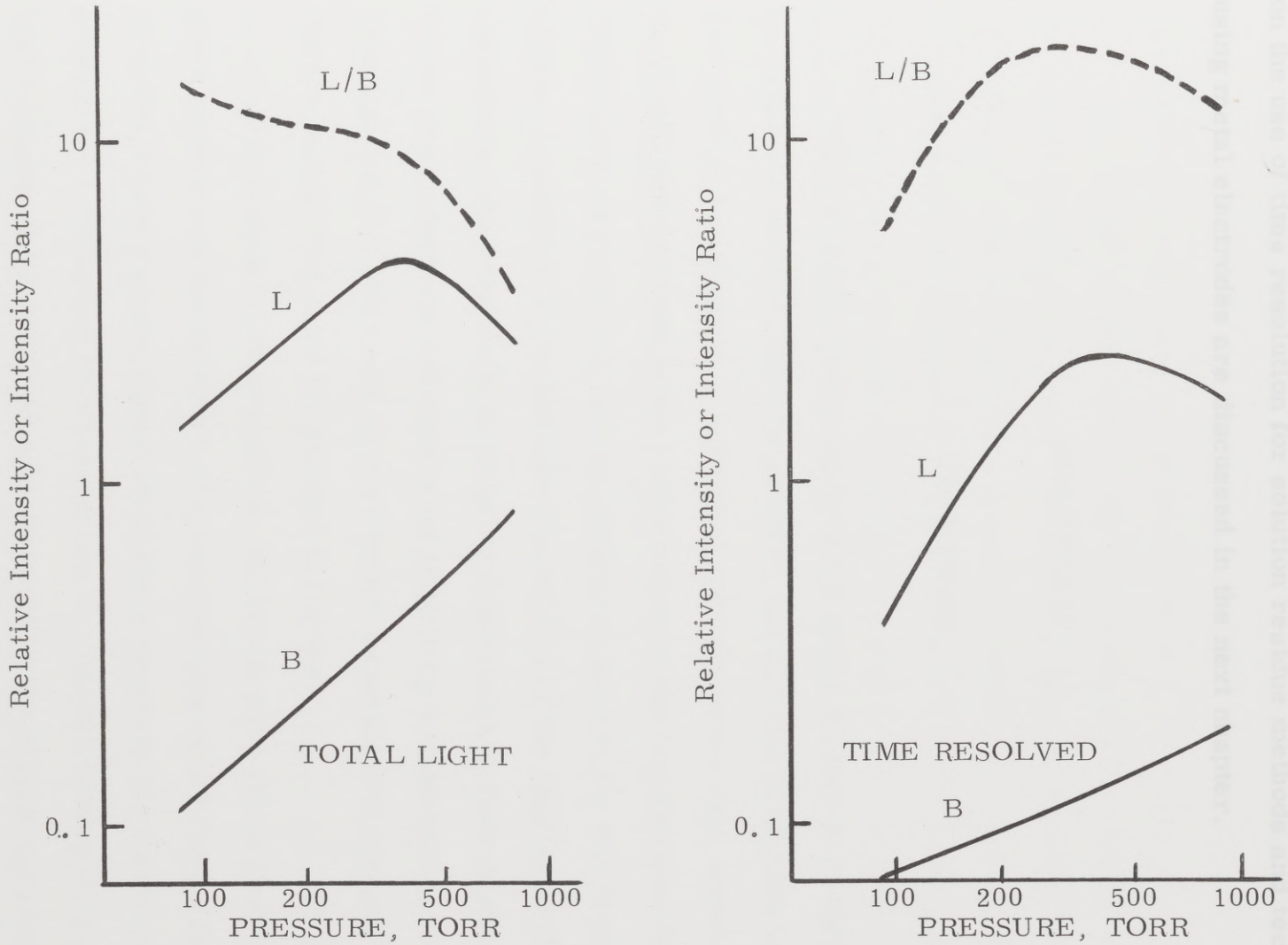


Figure 32. Relative intensity and intensity-ratio curves for CrII 2677.2 with pressure; Light sampled at midplane of 3 mm. gap; On-time, 20 $\mu$sec.

resolution is proportional to improvement in sensitivity. Several aspects on the use of time resolution for solution residue methods and techniques using metal electrodes are discussed in the next chapter.

# CHAPTER IV

## DISCUSSION

The use that has been made of the spark discharge in spectrochemical analysis can be further extended by use of time-resolution techniques. The study of the changes of individual species (molecular, atomic, and ionic) will provide fundamental information to the mechanisms for the vaporization of materials into the analytical gap and the excitation mechanisms. In addition to the fundamental studies of the physical and chemical phenomena, the possibility of utilizing differences in time-dependent behavior to an advantage for improving sensitivity are apparent. In this investigation the latter was considered by observing the changes in the line-to-background ratio for several variables.

For photographic recording, the background sets a limit for a given exposure in the detection of a spectral line of interest. This restriction means that one cannot indefinitely increase the exposure to compensate for a reduction in concentration to improve detectability. The high intensity of the continuous background is the determining factor for concentrational sensitivity with the spark discharge. It is shown that

time-resolved spectroscopy will improve the capabilities of spark excitation by the elimination of a great part of the continuous background. For any actual spectrograph, stray or scattered light is included in what is measured as the total background radiation.

The many variables that must be considered have been indicated in previous chapters. The sum of variables inherent in capacitor discharge circuits, excitation mechanisms, and those introduced by using time resolution permutes to many possible experiments for a given particular type of source. The unidirectional type of discharge used principally in this investigation represents only one of many types of discharges available for study. The effects of changes found with different atmospheres are undoubtedly determined by the composition of the atmosphere which may be a complex mixture in the case of air, an arbitrary binary mixture, or a "pure" gas containing very small amounts of impurity gases. The atmosphere compositions used in this investigation are representative of what may be of general practical application in the laboratory on a routine basis.

The graphite spark technique investigated here represents a special application of spark discharges to evaluate quantitatively amounts as small as $10^{-10}$ grams of an element. Its unusual sensitivity makes its study using various atmospheric combinations and time-resolution of special interest. For several elements investigated here, improvements in sensitivity can be achieved by time-sectoring, a procedure which could be adapted readily to many standard pieces of equipment. This procedure would permit detection by means of photographic or photoelectric recording. The use of a rotating mirror system is not readily adaptable to standard equipment. For the comparison of various experimental condi-

tions and relative detection limits, the line-to-background intensity ratio can be used. Although the measurement of random variations in line intensity and background intensity provides a more fundamental measurement of a signal-to-noise, the evaluation of the intensity ratios is usually valid for spectrochemical applications using photographic recording. Over the useful analytical range for spectrochemical procedures, using photographic recording, the uncertainty is usually proportional to the concentration so that the relative standard deviation is a constant. Random variations tend to increase with the total signal and it is for this reason that it is desirable to keep the unwanted radiation as low as possible. For a total light exposure which has been optimized for line-to-background ratio, the background measurement is the most important in terms of reproducibility of that measurement. If time-resolved exposures are optimized on this same basis, i.e., achieving the same reproducibility of the background, then the improvement in sensitivity will be determined by the increased signal in the time-resolved case. This improvement is the same as that found by comparing the line-to-background intensity ratios for total light and time-resolved exposures taken for a given set of experimental conditions.

The graphite spark technique offers a wide variety of possiblities for improving or controlling sensitivity through the choice of matrix element additives, gaseous atmosphere, pressure, and appropriate time parameters. It has been shown in this investigation that each of these parameters, as well as others, results in marked changes in the relative sensitivity for both total light and time-resolved exposures. Enhancement of the arc spectra results with the addition of gallium as a buffer. The addition of oxygen also changes the character of the late light as shown by

the comparison of the arc-to-spark ratio for total light and time resolved exposures. The time-intensity variations are marked for several gases that can be easily used in the laboratory with flow conditions. Pressure studies show that improved sensitivity can be achieved by operating at pressures reduced from atmospheric. Improvements in sensitivity of greater than an order of magnitude are possible by selection of the proper combination of parameters. The evaluations made here may be further extended by the use of a photomultiplier detector which is fundamentally a more sensitive detector. Using a more sensitive detector would allow the choice of on-times greater than 10 to 20 microseconds where the line intensity is diminished but the line-to-background or signal-to-noise ratio would be improved. The use of photomultiplier detectors has the additional advantage in that statistical methods may be more precisely applied to the results.

For techniques using metal electrodes where sampling limitations do not usually exist, there is a wider range of time variables for possible use to achieve an improved analytical result. As with the graphite spark technique, the gaseous atmosphere, pressure, source parameters, and time factors on a microsecond scale provide a wide range of variables for improving sensitivity. The use of inert atmospheres may become general practice for spectrochemistry because of beneficial effects. In some applications, the use of the inert atmosphere is beneficial by eliminating surface oxidation reactions which can be detrimental. However, some experiments carried out in air show that there can be enhancement effects probably resulting from the presence of oxygen. The presence of oxygen will influence the method of vaporization and excitation of the sample as

well as the background behavior. The different gases greatly influence the nature of the spectrum. Total light and time-resolved exposures provide a way to study the behavior of neutral atom excitation and ionic species excitation. Because the ionization and excitation of atoms is a function of time, time-resolved exposures provide a means for separating lines thus making it easier to assign the spectral lines to a given ionic species. For the rotating disk studies reported here, this is most pronounced when total light exposures are compared with those taken many microseconds after initiation of the spark. Large differences in excitation behavior are noted with a change in the composition range and type of alloys being analyzed. This is particularly pronounced when oxygen is present during excitation. Marked differences in the visual appearance of the spark burn were noted in this investigation when oxygen was added. There is a desire among spectrochemists to be able to analyze a wide range of materials from common working curves. Because of the differences noted when oxygen is present and the effects produced in argon, it is felt that excitation in argon offers the greatest possibilities for satisfying this desire. The fairly high continuum associated with argon excitation can be diminished by the use of time resolution.

For investigations using time resolution, exposures made with a rotating mirror system provide the best method for studying the emission characteristics of individual lines and background. The equipment can be arranged so that very short time phenomena can be studied with the sacrifice in the total microsecond interval of time that can be observed. Very high time resolution is required to study the phenomena occurring with the breakdown of the gap and to follow very short life-time species. For ana-

lytical applications, sectoring devices may be used to an advantage from information gained from the rotating mirror exposures. Comparisons of the line-to-background ratio of the late light to early light from rotating mirror exposure often show differences which may be a factor of 50 higher for the ratio in the late light versus that at early time. For analytical use, comparisons should be made with comparable total light exposures. If the proper interval of time is selected, it can be stated that there will always be some improvement in any spark procedure if time resolution is used. In some cases the factor of improvement may be so small as to make its use impractical because of the additional instrumentation and control required. In most spectrochemical applications, the best conditions are most often a compromise between a group of parameters which individually are not optimized. Additionally many of the variables are not independent and cannot be studied with total light exposures. Time-resolved spectroscopy provides an additional method for the study and optimization of these parameters.

Studies of spatial effects within the analytical gap could result in the further improvement for spark procedures. Regions of enhancement prevail for all types of discharge and time resolution provides one way to study them. The spatial effects are strongly determined by the type of source being used. It was for this reason that an attempt was made to simplify this problem by making observations at times after the current was extinguished. The comparative behavior of the spark in different atmospheres found in this investigation shows some differences from that found with oscillatory discharges where observations are taken during the oscillatory train of discharges. Any definite statements about advan-

tages of the unidirectional over the oscillatory discharge for time resolution will require further investigations.

The use of the photographic recording is almost a requirement if studies are to be made of many different lines in many matrices. For particular applications photoelectric recording with electronic switching devices can provide the same information. Each has its advantages; the photographic plate for the amount of information that can be stored and the unlimited number of correlations that can be made, the photomultiplier for its better sensitivity and precisions in terms of statistical analysis that can be made from the results.

From the results presented here and the discussion of further experiments of the many variables, it seems clear that an increasing number of investigators will use time-resolved spectroscopy as a fundamental tool to understanding and for the improvement of existing procedures using spark discharges.

# BIBLIOGRAPHY


Anan'ev, Yu. A. and Mak, A. A., Optika i Spektroskopiya (Eng. trans.) 12, 440 (1962).

Baer, W. K. and Hodge, E. S., Appl. Spectroscopy 14, 141 (1960).

Baker, C. A., United Kingdom Atomic Energy Authority, Research Group, Report AERE-R2926, 1959.

Bardocz, A., Nature 171, 1156 (1953).

Bardocz, A., VII Colloquium Spectroscopicum Internationale, Sept. 1958, Rev. Universelle des Mines 15, 344 (1959).

Bardocz, A., Spectrochim. Acta 7, 307 (1955).

Bardocz, A., Appl. Spectro. 11, 167 (1957).

Bardocz, A., Vanyek, U. M. and Voros, T., J. Opt. Soc. Amer. 51, 283 (1961).

Bardocz, A. and Varsanyi, F., Z. Naturforsch. 10a, 1031 (1955).

Beams, J. W., Phys. Rev. 33, 1086 (1929).

Beams, J. W., J. Opt. Soc. Amer. 13, 597 (1926).

Beams, J. W. and Brown, J. L., J. Opt. Soc. Amer. 11, 11 (1925).

Boyd, B. R. and Goldblatt, A., Appl. Spectroscopy 19, 22 (1965).

Brody, J. K., Faris, J. P. and Buchanan, R. F., Anal. Chem. 30, 1909 (1958).

Crosswhite, H. M., Steinhaus, D. W. and Dieke, G. H., J. Opt. Soc. Amer. 41, 299 (1951).

Cundall, C. M. and Craggs, J. D., Spectrochim. Acta 7, 149 (1955).

Dienum, H. and deBoer, F., Spectrochim. Acta 2, 318 (1944).

Enns, J. H. and Wolfe, R. A., J. Opt. Soc. Amer. 39, 298 (1949).

Fred, M., Nachtrieb, N. H. and Tomkins, F. S., J. Opt. Soc. Amer. 37, 279 (1947).

Grant, C. L., Dissertation, Rutgers University, University Microfilms Mic. 60-4233, 1960.

Hagenah, W. D., VII Colloquium Spectroscopicum Internationale, Sept. 1958, Rev. Universelle des Mines 15, 369 (1959).

Hagenah, W. D. and Laqua, K., ibid. 15, 361 (1959).

Hovis, W. A., J. Opt. Soc. Amer. 52, 649 (1962).

Kaiser, H. and Wallraff, A., Ann. d. Physik 5, 34 (1939).

Laqua, K. and Hagenah, W. D., VIII Colloquium Spectroscopicum Internationale, Sept. 1959, Schweizerische Arbeitsgemeinschaft fur Spektralanalyse, Luzern, H. R. Sauerlander and Co., Aarau, Switzerland, 1960.

Laqua, K. and Hagenah, W. D., Spectrochim. Acta 18, 183 (1962).

Laqua, K. and Hagenah, W. D., X Colloquium Spectroscopicum Internationale, Spartan Books, Washington, D. C., 1963.

Majkowski, R. F. and Joseph, B. W., Spectrochim. Acta 18, 77 (1962).

Malpica, J. T. M. and Berry, T. M., Gen. Elec. Rev. 44, 563 (1951).

Meggers, W. F. and Corliss, C. H. and Scribner, B. F., National Bureau of Standards Monograph 32-Part 1, 1961.

"Methods of Emission Spectrochemical Analysis", ASTM Publication, Philadelphia, Penna., 1964.

Morris, J. M. and Pink, F. X., ASTM Spec. Tech. Pub. No. 221, 1957.

Owens, E. B., Appl. Spectroscopy 13, 105 (1959).

Schreiber, T. P. and Majkowski, R. F., Spectrochim. Acta 12, 991 (1959).

Schroeder, W. W. and Strasheim, A., IX Colloquium Spectroscopicum Internationale, June 1961, Publication du Groupement pour Li Advancement des Methodes Spectrographiques (G. A. M. S.), Muray-Print, Paris, 1962.

Schuster, A. and Hemsalech, G., Trans. Roy. Soc. (London) 193, 189 (1900).

Steinhaus, D. W. and Crosswhite, H. M., "Methods of and Systems for Spectrochemical Analysis", U. S. Patent No. 2,744,438, May 8, 1956.

Steinhaus, D. W., Crosswhite, H. M. and Dieke, G. H., Spectrochim. Acta 5, 436 (1953).

Steinhaus, D. W., Crosswhite, H. M. and Dieke, G. H., J. Opt. Soc. Amer. 43, 257 (1953).

Strasheim, A., Appl. Spectroscopy 11, 76 (1957).

Strasheim, A. and Schroeder, W. W., VII Colloquium Spectroscopicum Internationale, Sept. 1958, Rev. Universelle des Mines 15, 331 (1959).

Sukhodrev, N. K. and Mandelstam, S. L., Opt. i Spektroskopiya 6, 723 (1959).

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